POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

Master of Science Course in Materials Engineering

Master of Science Thesis

Investigation of adhesion testing setups for electrodes in Li-ion battery cells

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Abstract

This thesis project investigates the best testing quality control setup to measure the adhesion of the interface coating/metallic foil of electrodes in lithium-ion battery cells. In fact, there is no specific standard (ISO/ASTM) for this kind of adhesion testing to date.

Firstly, a review of the literature concerning lithium-ion batteries and adhesion test methods is given. The importance of the coating adhesion of electrodes is described. In fact, it is a critical mechanical property of the electrodes as it affects the electrochemical lifetime, cycle performance and stability of battery cells.

Secondly, three different tests were studied in more detail: the 180° peel test, the 90° peel test and the z-direction pull test. Method development efforts were carried out, to find the best specimen preparation method and the best parameters to be used during each test.

Once this was finalised, Measurement System Analysis (MSA) studies were carried out on all three test methods to validate and compare the suitability of the method as a routine quality control inspection for battery manufacturing.

Finally, the outcome of the MSA studies, with practical considerations about the tests, were compared to make a decision on which adhesion test suits best the Quality Control laboratory at Northvolt.

Riassunto in italiano

Abstract

Il lavoro di tesi è stato svolto presso l'azienda svedese Northvolt, nella sede Northvolt Labs AB di Vasteras, all'interno del dipartimento di Quality Control.
Il progetto nasce dalla necessità da parte dell'azienda di trovare il miglior test e relativo setup per misurare l'adesione tra coating e substrato metallico negli elettrodi delle batterie a ioni litio. Infatti vi è un'assenza di uno standard specifico per tali misurazioni. È estremamente importante verificare l'adesione coating-substrato degli elettrodi delle batterie a ioni litio perché l'intercalazione e deintercalazione degli ioni Litio, (cicli di carica e scarica della batteria), porta a rigonfiamento e restringimento delle particelle di materiale attivo negli elettrodi. Ciò comporta la formazione di stress superficiali che possono portare a delaminazione del coating, con riduzione del contatto elettrico e, di conseguenza, della capacità e vita utile della batteria.

Il lavoro è iniziato con un primo periodo di revisione della letteratura che ha permesso di inquadrare l'argomento e gli obiettivi della tesi. Ha quindi permesso di comprendere quali siano i vari passaggi della produzione di una cella in cui sono stati evidenziati i parametri chiave che influenzano l'adesione per ogni step del processo produttivo. Questi sono tutti racchiusi all'interno della fabbricazione dell'elettrodo e in particolare negli step di Mixing, Coating, Drying (asciugatura) e Calendering (pressatura).

La seconda parte è coincisa con lo sviluppo dei migliori metodi di preparazione dei campioni per i vari test provati (il peel test a 90° e il pull test in direzione z). Tutti i test effettuati in questa sezione, come nell'intero progetto, sono stati realizzati su fogli di elettrodi, ottenuti da rulli di produzione conservati all'interno della "clean and dry room". In questa parte si è cercato di testare diversi metodi di preparazione dei campioni e diversi parametri del test per trovare il metodo che assicurasse migliore riproducibilità e affidabilità (minor variazione dei risultati ottenuti) in relazione alla facilità di svolgimento del test. Ci si è infatti interrogati sull'influenza delle diverse possibilità nella realizzazione dei provini, dei parametri utilizzati e dell'influenza del coating e dei nastri adesivi impiegati nei test, tra le altre cose.

L'ultima parte ha visto lo svolgersi di test per uno studio statistico (MSA, Measurement System Analysis) su tre metodi: i due menzionati in precedenza e il peel test a 180°, il cui metodo era stato sviluppato prima dell'avvio di questo progetto. Si è quindi andati ad effettuare un confronto sia a livello statistico dei risultati, sia a livello pratico delle metodologie di preparazione dei campioni e dello svolgimento del test stesso (semplicità, velocità, ecc.).

1.Introduzione

1.1. Introduzione alle batterie a ioni litio

La revisione della letteratura ha permesso di comprendere l'importanza dell'utilizzo delle batterie a ioni litio, i componenti di una batteria, il processo di fabbricazione con particolare riguardo alla fabbricazione degli elettrodi, ma soprattutto l'importanza di una buona adesione (coating/substrato) degli elettrodi e quali siano i test maggiormente utilizzati (sebbene non sia stato ancora sviluppato uno standard).

Il mercato delle batterie a ioni litio è stato stimato in 41.1 miliardi di dollari nel 2021 con un futuro incremento del 12.3% al 2030. Il grande sviluppo di queste batterie è legato alle ottime proprietà che possiedono. Vengono ampiamente impiegate nel mercato dei dispositivi portatili (PC, smartphone, ecc.), ma sta sempre più prendendo piede un loro utilizzo nel settore automotive, permettendo di contrastare l'utilizzo di combustibili fossili e in una certa misura, di conseguenza, anche il cambiamento climatico.

Una cella di una batteria a ioni litio è principalmente composta da: anodo (elettrodo negativo), catodo (elettrodo positivo), elettrolita e separatore, come mostra la figura A)

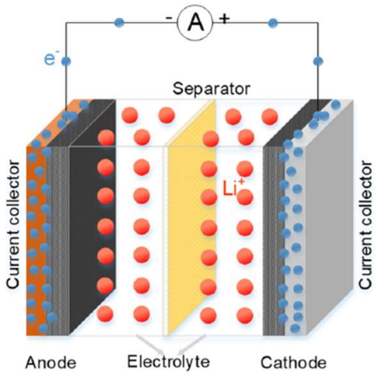


Figura A)

Il meccanismo di funzionamento delle batterie a ioni litio si basa sul principio di intercalazione reversibile degli ioni Li+ tra catodo e anodo. Nello stato di scarica il Litio è unicamente contenuto nel catodo. Durante la fase di carica, applicando quindi una corrente che fornisce elettroni all'anodo, gli ioni litio sono de-intercalati dallo strato catodico e trasferiti tramite l'elettrolita attraverso il separatore, nell'anodo. Nel processo di scarica, la migrazione degli ioni litio avviene in direzione contraria, con gli elettroni che passano nel circuito esterno per caricare vari dispositivi.

Diversi tipi di elettrolita vengono utilizzati, esempi sono DMC, EMC e DEC. Come separatore viene invece solitamente impiegata una membrana poliolefinica microporosa; la sua funzione è quella di evitare il contatto tra anodo e catodo, ma permettendo il passaggio degli ioni litio.

1.2 processo produttivo

Il processo di produzione di batterie si divide in tre grandi processi: produzione degli elettrodi, assemblaggio delle celle (cell assembly, CA) e finitura (attivazione della batteria). La parte più importante in riferimento a questo progetto di tesi è la fabbricazione degli elettrodi, in quanto i test di adesione sono effettuati su elettrodi pressati.

La produzione degli elettrodi si divide in diversi passaggi:

-Mixing: si divide ulteriormente in due step. Il primo a secco prevede il miscelamento del materiale attivo, solitamente grafite per l'anodo e Li-NMC per il catodo, un additivo conduttivo e un legante. Il secondo, a umido, prevede l'aggiunta di un solvente per ottenere uno slurry omogeneo. Diversi materiali vengono utilizzati per anodo e catodo: per il primo, SBR e CMC (binders) sono disciolti in acqua deionizzata (solvente). Per il catodo invece NMP (solvente) viene usato per disciogliere il legante che è solitamente PVDF. Il ruolo del legante è quello di prevenire la formazione di cricche, migliorando l'adesione e l'elasticità del coating.

-Coating: lo slurry viene depositato sulle lamine metalliche (metallic foils), Cu per anodo e Al per catodo, su entrambi i lati utilizzando uno slot die per ottenere una copertura uniforme. Il coating apporta miglioramenti su stabilità, conduttività e proprietà di adesione. Il coating può essere simultaneo su entrambi i lati oppure può essere fatto un lato per volta. La figura B) mostra un generico schema del processo di coating.

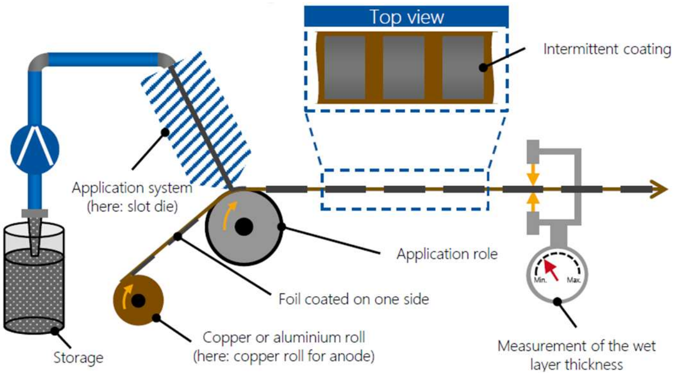


Figura B)

È stato dimostrato come un maggior quantitativo di legante vicino alla lamina metallica comporti una maggiore adesione, per cui sono allo studio elettrodi composti da diversi strati di coating, con strati a maggiore contenuto di legante più vicini all'interfaccia con la lamina metallica.

-Drying: questo processo di asciugatura viene effettuato in forni che permettono di andare a far evaporare il solvente. Il passaggio delle lamine viene solitamente effettuato tramite rulli. Si tratta di uno step molto importante riguardante l'adesione e i parametri da tenere maggiormente sotto controllo sono T e velocità di essicazione / asciugatura. In particolare, la velocità, se troppo elevata, può provocare la migrazione del legante, con conseguente riduzione dell'adesione.

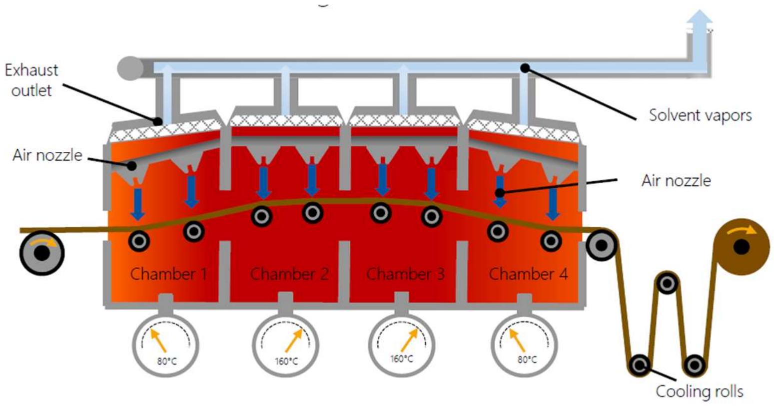


Figura C) rappresentazione dello step di essicazione

-Pressatura: è ottenuta tramite compressione dell'elettrodo da entrambi i lati utilizzando un paio di rulli rotanti. Questo step permette di ottimizzare alcune proprietà fisiche come porosità, densità e conduttività. Una riduzione delle porosità massimizza il contatto tra particelle portando ad un miglioramento, ad esempio, nella densità di energia. I parametri da tenere maggiormente in considerazione in questo step quindi, oltre alla pressione applicata, sono il diametro dei rulli e la temperatura a cui si sviluppa il processo.

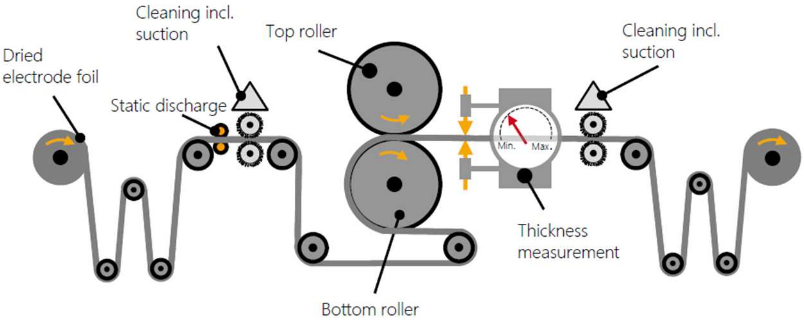


Figura D) rappresentazione dello step di pressatura

1.3 Adesione del coating

Perché l'adesione del coating è importante? Si tratta di una proprietà meccanica estremamente importante poiché ha un'influenza sulla stabilità delle batterie, sulle prestazioni e soprattutto sul ciclo di vita.
Il coating deve resistere alle ulteriori fasi del processo, ma soprattutto deve ovviamente resistere meccanicamente durante il servizio della batteria.
L'intercalazione e la de-intercalazione del litio (ciclo di carica e scarica) provoca dilatazioni di volume e ritiro delle particelle di materiale attivo, inducendo la formazione di sollecitazioni meccaniche. Il rigonfiamento porta, infatti, alla formazione di tensioni meccaniche all'interfaccia particella-legante che portano alla formazione di cricche, o delaminazione locale del rivestimento dal collettore di corrente compromettendo il contatto elettrico, provocando disomogeneità nella densità di corrente e diminuendo la stabilità del ciclo. Questo è il motivo per cui la forza di adesione del rivestimento influisce sulla durata e sulle prestazioni delle batterie.

Inoltre, il silicio è stato studiato intensamente ed è considerato un possibile futuro materiale per l'anodo, sostituendo la grafite come materiale attivo grazie alla sua elevata capacità specifica (10 volte maggiore della grafite). Il problema è che la sua espansione di volume è molto più alta (fino al 300%). Per questo motivo testare l'adesione del coating degli elettrodi risulta essere sempre più importante.

Tra i fattori più importanti che influenzano l'adesione si trovano: la composizione del coating (in particolare la quantità di legante e la sua distribuzione), lo spessore del rivestimento e i parametri relativi alle fasi di essiccazione e pressatura (T essiccamento, velocità di essiccamento, porosità finale, T di pressatura, ecc.).

Come testare l'adesione del coating degli elettrodi? Non esiste uno standard specifico approvato che permetta di avere una metodologia di test univoca. In letteratura si trovano diversi studi in cui viene impiegato il Peel test sia a 90° che a 180° gradi. Inoltre, è stata suggerita la possibilità di utilizzare il cosiddetto Pull test, che differisce dai due precedenti ma che potrebbe potenzialmente ridurre i tempi di test. Lo scopo di questo progetto è quello di andare a confrontare tali test per capire quale sia il più funzionale da effettuare nel dipartimento di controllo qualità dell'azienda.

Tutti e tre questi test vengono svolti utilizzando un "Tensile tester" o UTM (Universal testing machine), impiegando però diversi setup.

Peel test

Questo test prevede di andare ad applicare un nastro a bi-adesivo su un lato di un elettrodo. Si prepara lo strip che deve essere testato, andando a rimuovere o meno a seconda dei casi (e del test) lo strato di coating dal lato opposto a cui si è applicato il nastro. A quel punto si va ad incollare, grazie al nastro, il campione su una piastra rigida e questa si incastra nell'apparecchiatura inferiore del test. Quest'apparecchiatura è diversa per i due test a 90° e 180°, mentre il grip superiore è identico in entrambi i casi. A questo punto la lamina metallica viene parzialmente staccata dal coating sottostante e viene fissata nel grip superiore. A seconda dell'apparecchiatura utilizzata l'angolo che si formerà sarà a 180° o a 90° gradi come mostrano rispettivamente le figure E), F).

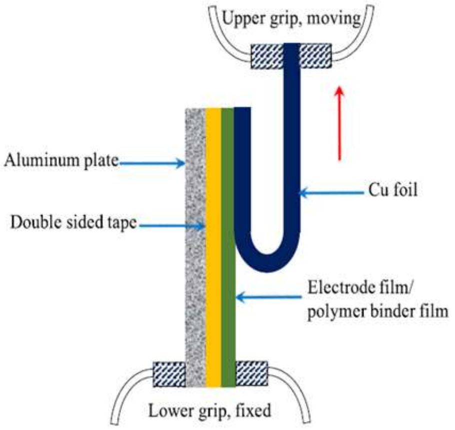


Figura E) Rappresentazione schematica di un Peel test a 180°

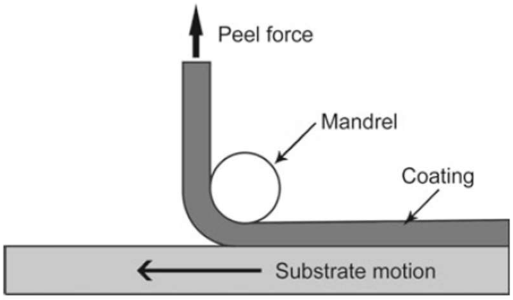


Figura F) Rappresentazione schematica di un Peel test a 90°

La forza di adesione misurata durante il test è influenzata da diversi parametri come la velocità di peeling e l'angolo e dalle condizioni in cui avviene la misurazione T, umidità, ecc.

Il problema del peel test è che si ha un contributo legato alla deformazione della lamina metallica nel valore registrato della forza di adesione e che dipende dall'angolazione a cui viene effettuato il peel off della lamina stessa. Uno studio [Gent et al.] ha inoltre dimostrato come il contributo di sia molto inferiore per il Peel test a 90° rispetto a quello a 180°, e per questo motivo il primo viene considerato come un test che restituisce una misura più "pulita".

Pull test in direzione Z

Come già menzionato, anche per questo test è necessario disporre di un "tensile tester", ma l'apparecchiatura utilizzata è diversa da quella del peel test. In questo caso si applica il nastro bi-adesivo su un lato dell'elettrodo, si taglia la strip da testare e si incolla tramite il nastro al grip inferiore dell'apparecchiatura. Si applica altro nastro sul grip superiore e poi si tagliano i cinque segmenti del grip. Con questo test, infatti, si riescono ad effettuare 5 misurazioni per strip preparata. Ogni strip di elettrodo viene suddivisa in 5 quadratini permettendo di effettuare la misurazione cinque volte. Una volta preparato il setup, si avvia il macchinario che andrà a comprimere inizialmente l'elettrodo tra i due grip e successivamente vi sarà lo step di "pull off" in cui si avrà separazione tra il laminato metallico e il coating, e il macchinario andrà a registrare la forza necessaria alla separazione.

Ci sono moltissimi parametri del test che possono essere variati: tempo di compressione, forza di compressione, velocità di test, ecc.

Questo test è efficace quando l'adesione tra coating e substrato non è troppo elevata, essendo la forza adesiva del nastro il fattore limitante.

Durante un test di pull-off ad esempio si possono osservare tre modalità di frattura, come mostrato nella figura G)

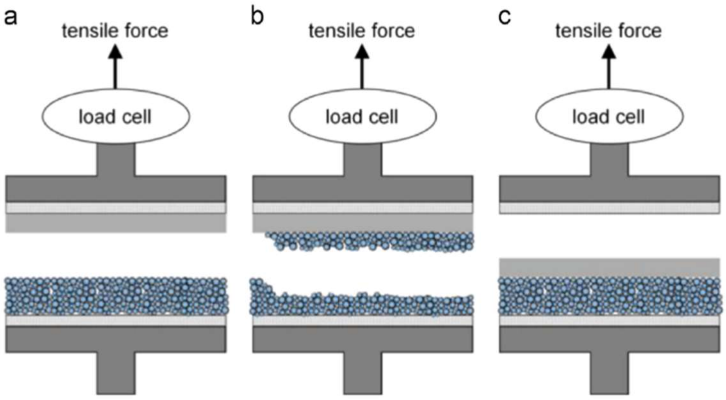


Figura G) rappresentazione delle modalità di frattura osservabili durante un pull test.

La rottura rappresentata in a vene definita frattura di tipo adesivo, in questo caso si riesce quindi a determinare in maniera efficace la forza adesiva tra coating e substrato metallico. La rottura rappresentata in b viene invece definita frattura di tipo coesivo; una combinazione tra frattura adesiva e coesiva è anche possibile. Quando il DoR (Degree of removal) è maggiore del 95%, la frattura viene detta adesiva. La terza, c, riguarda un fallimento dell’adesivo, si tratta di quel fattore limitante menzionato in precedenza; in questo caso l’interfaccia coating substrato è più forte di quella tra coating e adesivo.

2.Sviluppo dei vari metodi

La seconda parte del progetto è consistita nel cercare il miglior metodo di preparazione dei campioni e il miglior “test method” (parametri, nastri, ecc.) per il peel test a 90° e il pull test in direzione z in modo da minimizzare le variazioni nei risultati.

Tutti gli esperimenti effettuati in questa sezione sono stati fatti su fogli di anodo pressati.

Recap sui materiali dell’anodo: il foil è in Rame, il materiale attivo è grafite, il binder è CMC (aggiunta spesso di SBR) e il solvente è acqua deionizzata.

Sono stati utilizzati due tipologie di nastro biadesivo Per il nastro 3M il “backing material” è in “treated paper” con adesivo in “natural rubber”. Per il nastro tesa, film in PVC con adesivo in “tackified acryilic”.

2.1.sviluppo 90°

2.1.1.Nozioni già note dal peel test a 180°

Il peel test a 180° era stato già sviluppato e validato prima dell’inizio di questo progetto e siccome il 90° peel test è simile, si è cercato di sfruttare quanto già noto da esso. La preparazione dei campioni è stata mantenuta pressoché identica. Si è cercata un’alternativa a questo test perché nella procedura di preparazione del campione un lato del coating deve essere rimosso, richiedendo un lungo tempo di preparazione dei campioni. La letteratura suggerisce che, essendo l’angolo utilizzato nel 90° peel test inferiore, il contributo della deformazione della lamina alla forza registrata sia inferiore, permettendo di ottenere una misura più “pulita” e quindi suggerendo la possibilità di poter lasciare il coating durante la misurazione.

2.1.2.Effetto della presenza/assenza del coating sui campioni testati

Si è quindi investigata la possibilità di lasciare il coating sul campione. 24 misurazioni sono state effettuate: 12 sul lato A (6 con coating e 6 senza) e 12 sul lato B (6 con coating e 6 senza).

Già solo dai grafici, per entrambi i lati, si è notata una minor linearità delle curve per i campioni testati senza rimozione del coating. I dati hanno poi confermato questa prima osservazione: per entrambi i lati i campioni testati con il coating la deviazione standard è risultata molto maggiore di quella dei campioni testati senza coating. Inoltre, i valori ottenuti nelle misurazioni con coating sono risultati essere nettamente maggiori di quelli senza il coating (circa il triplo). Questo ha portato a concludere che le misurazioni dei campioni con entrambi i lati del coating non permettano di misurare l'effettiva forza di adesione tra coating e substrato. Inoltre, i dati suggeriscono sia opportuno rimuovere il coating anche per questo test.

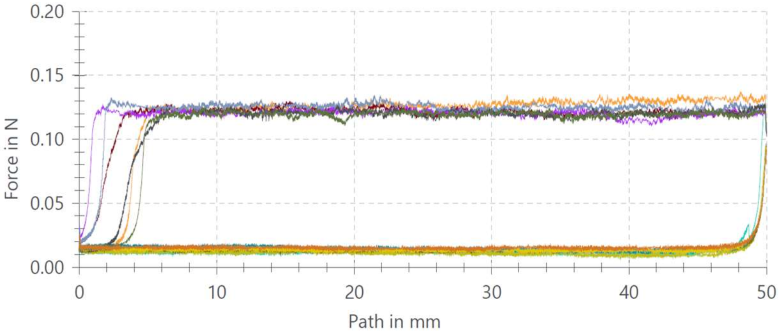


Figura H) Grafico del peel test a 90 (lato B) con rimozione di un lato del coating

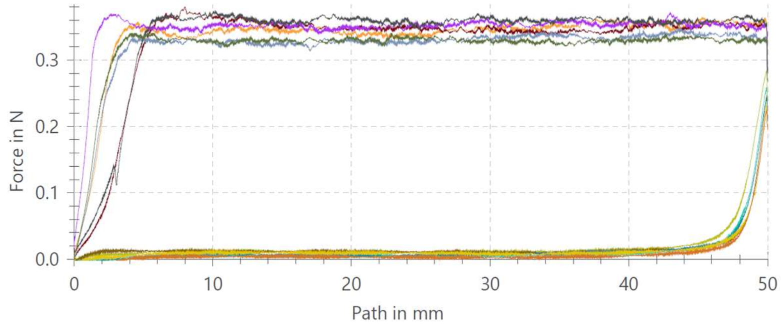


Figura I) Grafico del peel test a 90 (lato B) senza rimozione di un lato del coating

2.1.3.Possibile influenza del nastro bi-adesivo

Si è inoltre cercato di capire se il tipo di nastro bi-adesivo influenzasse la misurazione e pertanto sono state svolte altre 24 misurazioni usando una diversa tipologia di nastro. 12 test sono stati effettuati sul lato A senza coating e 12 con. I valori registrati per i campioni testati senza coating sono coerenti con i valori ottenuti per il precedente nastro, indicando che il nastro non influisce sulla misurazione almeno quando si rimuove il coating. Anche in questo caso i valori registrati dei campioni con coating sono risultati molto maggiori di quelli senza, ma questa volta sono circa 5 volte maggiori. Anche in questo caso la deviazione standard dei campioni con coating è molto maggiore di quelli senza, confermando la necessità di andare a rimuovere il coating.

Tab.a Risultati lato A con entrambi i nastri

	A side uncoated 3M (6 measurements)	A side uncoated Tesa (12 measurements)	A side coated 3M (6 measurements)	A side coated Tesa (12 measurements)
Force avg [N]	0.091	0.086	0.286	0.400
Standard deviation	0.0036	0.004	0.0087	0.0194

2.2.Sviluppo pull test in direzione z

2.2.1.Introduzione al test

Il test consiste nel posizionare un pezzo di nastro biadesivo su un lato dell'elettrodo. Questo viene poi tagliato, pressato e fatto aderire ad uno dei due grip utilizzati per il test. Sull'altro grip si applica un'altra striscia di nastro bi-adesivo. I grip vengono quindi montati sul macchinario e il test consiste in una prima parte di compressione e una seconda in cui viene effettuato il cosiddetto "Pull off". Alla fine si possono ottenere due situazioni:

1. -distacco coating lato A-foil
2. -distacco coating lato B foil

La situazione 1 è quella che si presenta maggiormente. Infatti è noto che, a causa del processo produttivo, l'interfaccia coating lato A-foil sia quello più debole e quello che dovrebbe subire sempre distacco. Le immagini J, K, L rappresentano questi concetti.

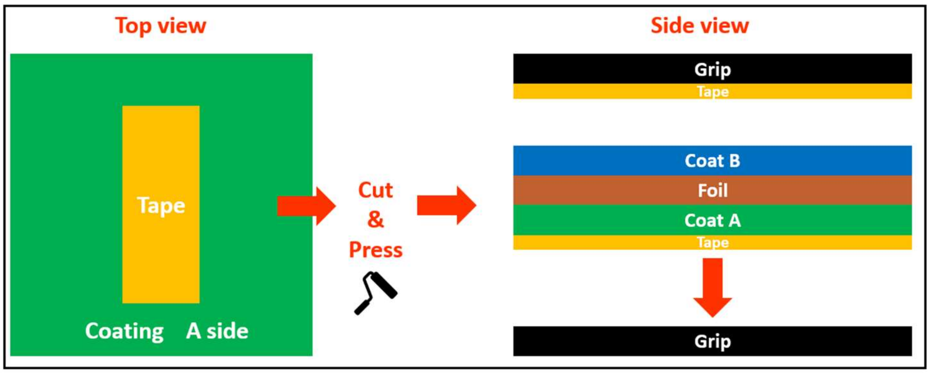


Figura J) Rappresentazione del processo di ottenimento del campione e adesione ai grip

Figura K) Rappresentazioni delle fasi di compressione pull off del test

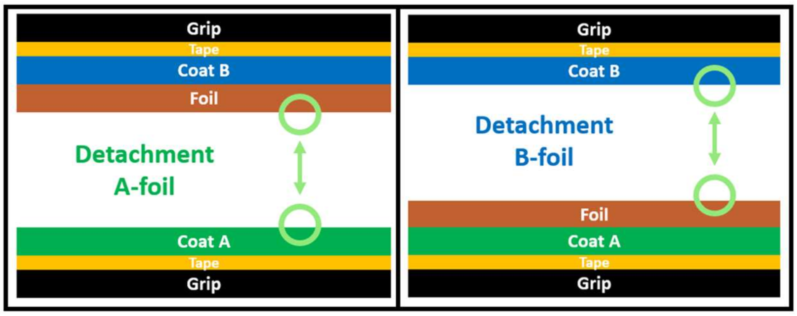


Figura L) Rappresentazione dei due possibili scenari alla fine del test

2.2.2.Effetto dei mezzi di preparazione dei campioni e ordine dei passaggi

Quattro metodi di preparazione sono stati investigati principalmente. In tutti i casi il primo passaggio è quello di far aderire il nastro bi-adesivo sull'elettrodo, questo viene poi tagliato e pressato con diversi mezzi e in un diverso ordine cronologico a seconda del metodo:

1. “Method 1”: il taglio viene effettuato tramite una pressa e un cutting die e pressato con il “big roller” prima di essere posizionato sul grip.
2. “Method 2”: il taglio viene effettuato come nel metodo 1 ma questa volta si fa aderire prima l’elettrodo al grip e successivamente pressato, questa volta con il “little roller”
3. “Method 3”: in questo metodo il taglio viene effettuato con un normale cutter e successivamente per la pressatura si segue lo stesso principio del primo metodo.
4. “Method 4”: anche in questo caso si utilizza il cutter e si segue per la pressatura lo stesso principio del metodo 2.

Le immagini M e N riassumono i principali step dei 4 metodi.

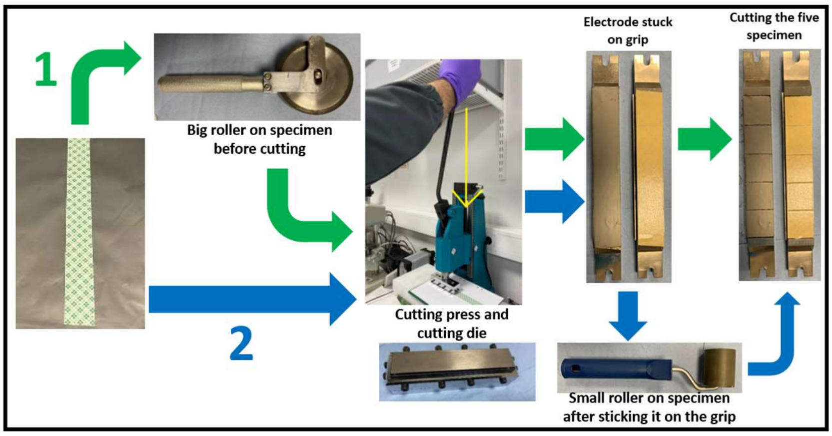


Immagine M) Successione dei vari step per il method 1 e 2.

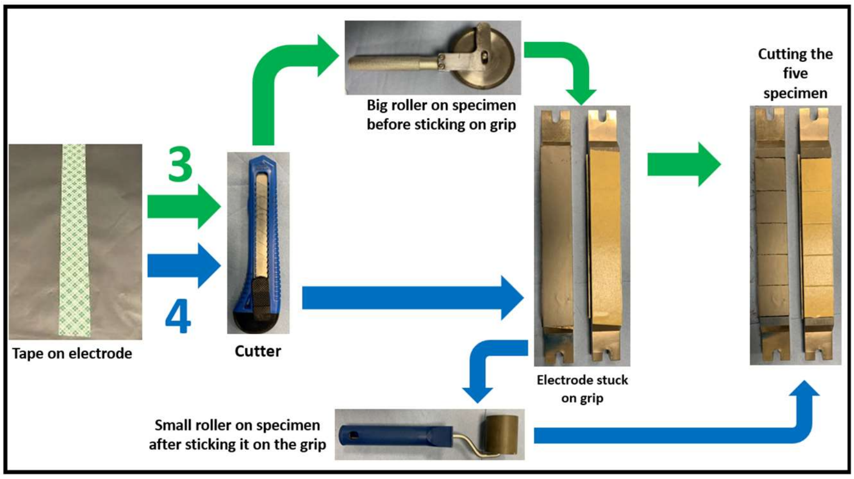


Figura N) successione dei vari step per il metodo 3 e 4

Per investigare il miglior metodo di preparazione sono stati effettuati 3 set di esperimenti in tre diversi giorni, usando per ogni set fogli di elettrodo provenienti da un diverso roll, ma in ogni set fogli dello stesso roll sono stati indagati con tutti i metodi. La seguente tabella riassume tutti i risultati ottenuti.

Tab. b risultati delle misurazioni per comprender il miglior metodo di preparazione del campione

	Method 1	Method 2	Method 3	Method 4
Avg Force set 1	166.1	161.1	149.2	150.6
Avg Force set 2	174.1	168.7	158.9	164.9
Avg Force set 3	128.3	125.4	123.6	116.5
Sdev set 1	7.9	9.9	11.3	11.3
Sdev set 2	9.5	12.2	24.4	15.1
Sdev set 3	20.8	13.7	18.1	15.7

Failures set 1	0/4	0/4	0/5	0/4
Failures set 2	3/12	0/12	3/14	2/14
Failures set 3	4/12	0/12	5/14	0/14
Overall Avg Force	156.1	151.7	143.9	144.0
Avg Sdev	12.7	11.9	18.0	14.0
Avg Sdev%	8.2	7.9	12.5	9.8
Total number of failures	7/28	0/28	8/33	2/ 32
% of failures	25	0	24.2	6.3

In conclusione, siccome il metodo 2 presenta i minori valori di deviazione standard e di “failures” (distacco non omogeneo del coating) è il metodo raccomandato e che verrà adottato durante l’MSA per la validazione del processo.

2.2.3.Effetto del posizionamento del nastro bi-adesivo sul lato A o B

Per comprendere su quale lato dell’elettrodo fosse più opportuno applicare il nastro (A, come mostrato nella figura J, o B), sono state effettuate 35 misurazioni per lato su fogli provenienti dallo stesso roll.

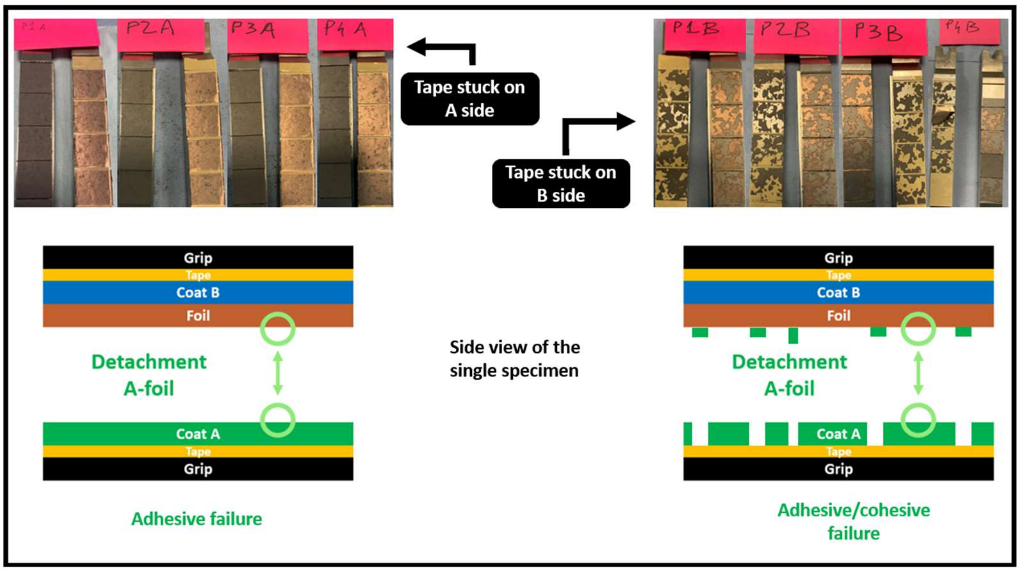


Figura O) Campioni testati applicando il nastro biadesivo sul lato a (sx) e sul lato B (dx) con relativa rappresentazione della sezione del singolo campione.

Tabella c. Risultati delle misurazioni

	Side A	Side B
Number of failures	3/35	1/35
Avg max. tensile force [N]	156.453	122.7

La tabella mostra i risultati ottenuti applicando il nastro su entrambi i lati, ma i valori numerici non sono in realtà stati presi in considerazione. Infatti, già a livello visivo ci si è resi conto, sebbene si raggiunga il corretto distacco tra coating A e foil nella quasi totalità dei test per entrambi i casi, di come si ottenga un risultato nettamente migliore (maggiore omogeneità) applicando il nastro sul lato A. Nella figura O si può osservare tutto ciò. I valori numerici hanno comunque confermato ipotizzato già a livello visivo: il valor medio è inferiore quando il nastro viene applicato sul lato B, infatti in questo caso non si riesce ad ottenere il valore effettivo dell’adesione coating-substrato, ma si registra un valore dovuto ad un mix di “adhesive/cohesive failure”.

2.2.4.Effetto dei parametri

Quattro diversi setup di parametri sono stati investigati. La tabella d riassume le principali differenze. Mentre la tabella e riporta i risultati.

Tabella d Elenco dei parametri per i diversi setup

	Setup 1	**Setup 2**	**Setup 3**	**Setup 4**
Compressive stress	0.5 MPa	0.5 MPa	0.6 MPa	0.6 MPa
Dwell time	6 s	6 s	30 s	30 s
Test speed	10 mm/min	100 mm/min	10 mm/min	100 mm/min
Data acquisition rate	2 kHz	2 kHz	2 kHz	2 kHz

Tabella e. Risultati dei test effettuati utilizzando i diversi setup

	Setup 1	Setup 2	Setup 3	Setup 4
Avg max. tensile force [N]	151.7	-	138.9	-
Avg Sdev	11.9	-	20.3	-
Sdev%	7.8	-	14.6	-
Total failures	0/28	8/8	9/12	8/8
%failures	0	100%	75%	100%

In conclusione, gli unici parametri che hanno permesso di ottenere un numero accettabile di non-failures sono quelli utilizzati nel setup 1.

2.2.5.Effetto delle tipologie di nastro bi-adesivo

Per verificare se vi sia un'influenza da parte del tipo di nastro sul test, un diverso tipo di nastro bi-adesivo (Tesa®) è stato utilizzato. Sono stati quindi effettuati alcuni test utilizzando diversi setup, giungendo alla conclusione che il miglior setup sia il 4. Il fatto che per i due nastri i migliori setup siano diversi fa già intuire che ci possa essere un'influenza da parte del tipo di nastro.

Sono stati quindi effettuati dei test utilizzando i migliori parametri di ciascun nastro per entrambi i nastri. La tabella f mostra i risultati.

Tabella f. Risultati dei test effettuati su entrambi i nastri con i setup 1 e 4.

	Tesa		3M	
	Method 2 Setup 1	**Method 2 Setup 4**	**Method 2 Setup 1**	**Method 2 Setup 4**
Avg max. tensile force [N]	283.7	412.9	151.7	(90.6)
Sdev	13.1	10.8	11.9	(14.4)
Sdev%	4.6	2.6	7.9	(15.9)
Number of failures	5/12 (41.67%)	1/12 (8.34%)	0/28	8/8 (100%)

È possibile notare la grossa differenza nel valor medio della massima forza di trazione registrata, concludendo che vi è un'influenza da parte del tipo di nastro. Non è però chiaro in che modo questo nastro possa influire in maniera così sostanziale sulla forza registrata.

Sono quindi state effettuate delle misurazioni solo sui nastri: si è inserito il nastro su un grip e si è andato ad effettuare pull test in direzione z, per entrambi i nastri con i setup 1 e 4.

Figura P) Pull test in direzione z effettuato sui nastri.

Tabella g. Risultati dei pull test sui nastri

	3M		Tesa	
	Setup 1	**Setup 4**	**Setup 1**	**Setup 4**
Avg max tensile Force [N]	272.4	603.5	465.1	1130.1
Sdev	10.0	24.9	11.0	42.7
Sdev%	3.7	4.1	2.4	3.9

Da questi risultati si evince come il nastro Tesa abbia una forza adesiva nettamente superiore e che il setup 4 porti a risultati della massima forza adesiva registrata molto più alti. Si deve però tenere conto del fatto che non è detto che il Tesa (essendo i materiali dei due nastri diversi tra loro) abbia una forza adesiva superiore anche sull'elettrodo, poiché ovviamente il materiale del grip e del coating sono molto diversi e potrebbero reagire in maniera diversa a seconda del tipo di adesivo del nastro.

2.2.6.Effetto dei campioni con e senza coating con entrambi i nastri

Per cercare di comprendere se il coating influenzi le misurazioni (come avviene nel caso del peel test) sono stati effettuati test utilizzando entrambi i nastri (ciascuno con il proprio miglio setup) su campioni con e senza coating. La tabella f riporta i risultati.

Tabella f Risultati dei test su campioni con e senza coating

	Tesa (Method 2 Setup 4)		**3M** (Method 2 Setup 1)	
	Coated	**Uncoated**	**Coated**	**Uncoated**
Avg max. tensile force [N]	436.1	378.5	179.9	166.9
Sdev	23.8	20.1	12.4	5.9
Sdev%	5.4	5.3	6.9	3.6
Number of failures	0/5	0/6	1/6	0/5

La rimozione del coating è stata molto più omogenea nel caso dei campioni a cui era stato rimosso un lato del coating, nei test usando il nastro 3M. questo effetto non si osserva utilizzando il nastro Tesa perché si ha omogenea rimozione del coating in entrambi i casi. Però nel caso del nastro Tesa vi è una differenza maggiore nel valor medio della forza registrata, rispetto ai test effettuati con nastro 3M. questo sembra suggerire una certa influenza del coating solo nei test con nastro Tesa, ma uno studio utilizzando un maggior numero di campioni andrebbe eseguito per poter effettuare conclusioni più approfondite.

2.3.Conclusioni sullo sviluppo del metodo

Il prossimo step del progetto è stato quello di effettuare un Measurement System Analysis (MSA) per ogni metodo sviluppato in modo da validarlo. Per il 90° peel test verrà effettuato su campioni a cui verrà rimossa un lato del coating. Tuttavia un MSA anche su campioni con coating da entrambi i lati sarà effettuato per avere un buon paragone tra i metodi. Verrà effettuato un MSA anche per il 180° peel test per andare ad effettuare un confronto con il 90° peel test.

Infine, un MSA sarà effettuato per il pull test in direzione z. sarà da effettuare con il "metodo 2 setup1" nel caso si utilizzi il nastro 3M, con "metodo 2 setup4" nel caso si utilizzi il nastro Tesa. Se si effettuasse per entrambi i nastri si potrebbe avere un ulteriore confronto che possa permettere di capire meglio quale sia più conveniente in termini di variabilità dei risultati.

3.Measurement System Analysis (MSA)

3.1Introduzione al MSA

I sistemi di misurazione possono produrre risultati inaffidabili portando a cattive decisioni. Pertanto, il sistema di misurazione deve essere giudicato come affidabile prima di poter prendere decisioni basate su dati registrati con tale metodo di misurazione.

Un MSA è una serie di test che permettono di determinare se il sistema di misurazione sia affidabile in termini, tra gli altri, di variabilità. Questa si basa su due aspetti:

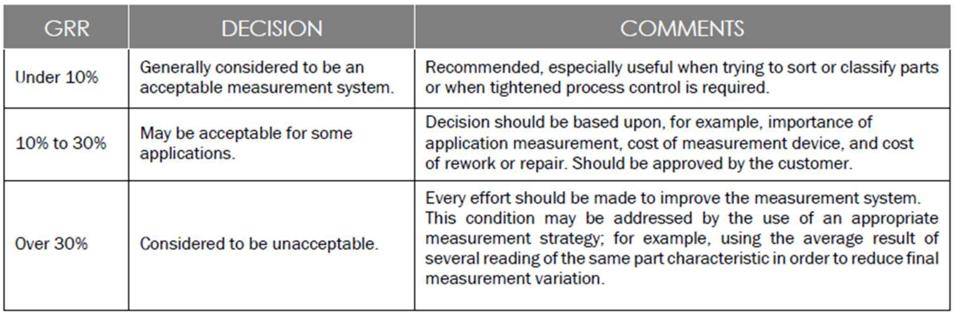
-ripetibilità ("repeatability"): è la capacità del sistema di misurazione di restituire gli stessi valori quando un operatore effettua diverse misurazioni sulla stessa unità. È quindi la variazione osservata quando lo stesso operatore misura la stessa unità diverse volte, nelle stesse condizioni.

-riproducibilità: è la variazione osservata quando più operatori misurano la stessa caratteristica sulla stessa unità, nelle stesse condizioni. È la variazione dovuta al sistema di misurazione.

Gauge Repeatability and Reproducibility (GR&R) test

Il GR&R test è un test che può essere condotto per determinare se esista un'eccessiva variabilità nel sistema di misurazione. Il criterio di accettabilità di questo test è mostrato nella tabella g.

Tabella g. Criteri di accettabilità dello studio GR&R



GRR	DECISION	COMMENTS
Under 10%	Generally considered to be an acceptable measurement system.	Recommended, especially useful when trying to sort or classify parts or when tightened process control is required.
10% to 30%	May be acceptable for some applications.	Decision should be based upon, for example, importance of application measurement, cost of measurement device, and cost of rework or repair. Should be approved by the customer.
Over 30%	Considered to be unacceptable.	Every effort should be made to improve the measurement system. This condition may be addressed by the use of an appropriate measurement strategy; for example, using the average result of several reading of the same part characteristic in order to reduce final measurement variation.

Due tipologie di questo test sono possibili per sistemi di misurazione distruttivi:

-Crossed Gage R&R study: in questo studio ogni operatore misura ogni parte; è chiamato crossed perché ogni operatore misura la stessa parte più volte. Sono necessari 3 operatori, 5 batch e un minimo di due campioni per operatore per ogni batch. Per ogni operatore vi è quindi un minimo di 10 misurazioni, per un minimo totale di 30 misurazioni.

-Nested Gage R&R study: in questo studio, ogni parte è unica, gli operatori non misurano la stessa parte. Sono necessari 3 operatori, 15 batch (5 ciascuno) e un minimo di due campioni per batch. Per ogni operatore vi è quindi un minimo di 10 misurazioni, per un minimo totale di 30 misurazioni.

Il programma utilizzato per calcolare i risultati di questi studi è stato Minitab®.

3.1.Primo set di studi MSA

Nel primo set di esperimenti è stato seguito lo studio "Nested", utilizzando quindi 15 diversi batch. Gli operatori hanno eseguito gli esperimenti da fogli provenienti sempre dagli stessi 5 batch (rulli) ciascuno.

3.2.1 90 peel test uncoated

La total Gage R&R ottenuta è stata del 61,45%, questo significa che il sistema di misurazione non è accettabile. La variabilità di questo studio proviene per la maggior parte dalla riproducibilità

(47.61%), ma un numero elevato è osservato anche per la ripetibilità (38.85%). Il report grafico ottenuto attraverso.

3.2.2.90 peel test coated

Anche se già durante lo sviluppo del metodo si era sconsigliato di mantenere un lato del coating per il test, si è preferito effettuare uno studio anche in questo caso per avere un ulteriore confronto e auspicabilmente una ulteriore conferma.

La total Gage R&R ottenuta è stata dell'87.34%, questo significa che il sistema di misurazione non è accettabile. La variabilità di questo studio proviene per la maggior parte dalla riproducibilità (82.10%), nettamente inferiore invece il valore della ripetibilità (29.80%).

3.2.3.180 peel test uncoated

Anche se questo peel test era già stato validato, si è preferito effettuare nuovamente lo studio per avere un metro di confronto quando gli stessi operatori hanno effettuato i test su fogli proveniente sempre dagli stessi rulli (operatore 1 rulli 1-5; operatore 2 rulli 6-10; operatore 3 rulli 11-15).

La total Gage R&R ottenuta è stata del 78.09 %, questo significa che il sistema di misurazione non è accettabile. La variabilità di questo studio proviene per la maggior parte dalla riproducibilità (71.78%), nettamente inferiore invece il valore della ripetibilità (30.76%).

3.2.4.Confronto del peel test a 90 coated/uncoated

Tabella h. Confronto tra valor medi ottenuti con i due test, deviazioni standard e deviazioni standard del range

	90° coated Adhesion Force [N]	90° coated Sdev range	90° uncoated Adhesion Force [N]	90° uncoated Sdev range	Difference in Adhesion Force [N]	Difference % in Adhesion Force
Op.3						
Avg	0.3546	0.0034	0.1016	0.002	0.253	55.46
Sdev	0.0086		0.0058			
Sdev%	2.43		5.70			
Op.1						
Avg	0.376	0.0036	0.1058	0.0021	0.270	56.08
Sdev	0.019		0.0047			
Sdev%	4.98		4.43			
Op.2						
Avg	0.3197	0.0034	0.0969	0.0026	0.2228	53.48
Sdev	0.0238		0.0076			
Sdev%	7.45		7.91			

Osservazioni:

-Il valor medio dei campioni con coating è molto maggiore. Questo era stato già notato durante lo sviluppo del metodo ed è legato al fatto che è richiesta più energia per piegare il foil con coating che senza e quindi il valore della forza registrato sarà maggiore.

-I valori della forza di adesione sono paragonabili per tutti gli operatori per i campioni senza coating. Quelli con il coating hanno mostrato invece una variazione maggiore e questo si può chiaramente notare dal grafico in figura Q).

-La deviazione standard in valore assoluto è sempre inferiore per campioni senza coating.

-La deviazione standard del range è nettamente inferiore per i campioni senza coating

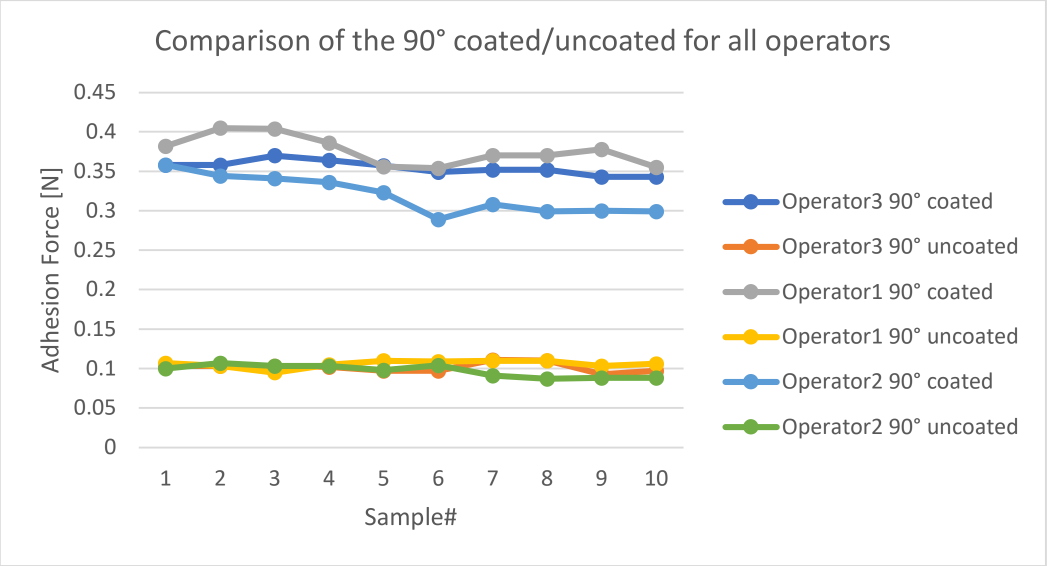


Figura Q) Grafico sul confronto per tutti gli operatori del peel test a 90 con e senza coating

3.2.5.Confronto peel test 90-180 uncoated

Tabella i. Confronto tra valor medi ottenuti con i due test, deviazioni standard e deviazioni standard del range

	180°Adhesion Force [N]	180° Sdev range	90°Adhesion Force [N]	90° Sdev range	Difference in Adhesion Force [N]	Difference % in Adhesion Force
Op.3						
Avg	0.0682	0.0012	0.1016	0.002	0.0334	19.67
Sdev	0.0017		0.0058			
Sdev%	2.47		5.70			
Op.1						
Avg	0.0737	0.0016	0.1058	0.0021	0.0321	17.88
Sdev	0.0064		0.0047			
Sdev%	8.75		4.43			
Op.2						
Avg	0.0618	0.0015	0.0969	0.0026	0.0351	22.11
Sdev	0.0058		0.0076			
Sdev%	9.37		7.91			

Osservazioni:

-La deviazione standard del range è inferiore per il peel test a 180

- Osservando la deviazione standard di tutti gli operatori, non si nota nessun trend, suggerendo che i due test siano quindi comparabili.

-Il valor medio della forza è inferiore per tutti e 3 gli operatori, per il test a 180. Questo è in accordo con quanto suggerito dalla letteratura. Si ipotizzava infatti che un angolo inferiore potesse avere un minor contributo dalla deformazione del foil e restituire una misura più "pulita". Si è provato ad evidenziare le forze agenti nei due test (figura R). Nel peel test a 90 gradi si misura solo la "tension" (pure mode 2); mentre nel 180 si hanno due contributi (tension + shear).

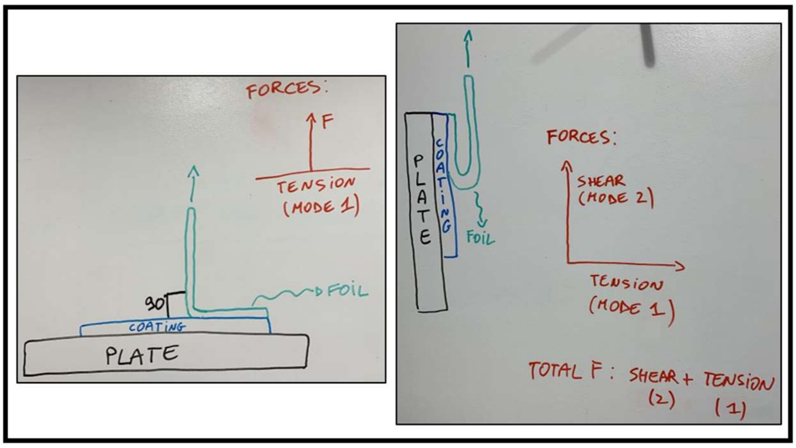


Figura R) Rappresentazione dei due test e delle relative forze in gioco

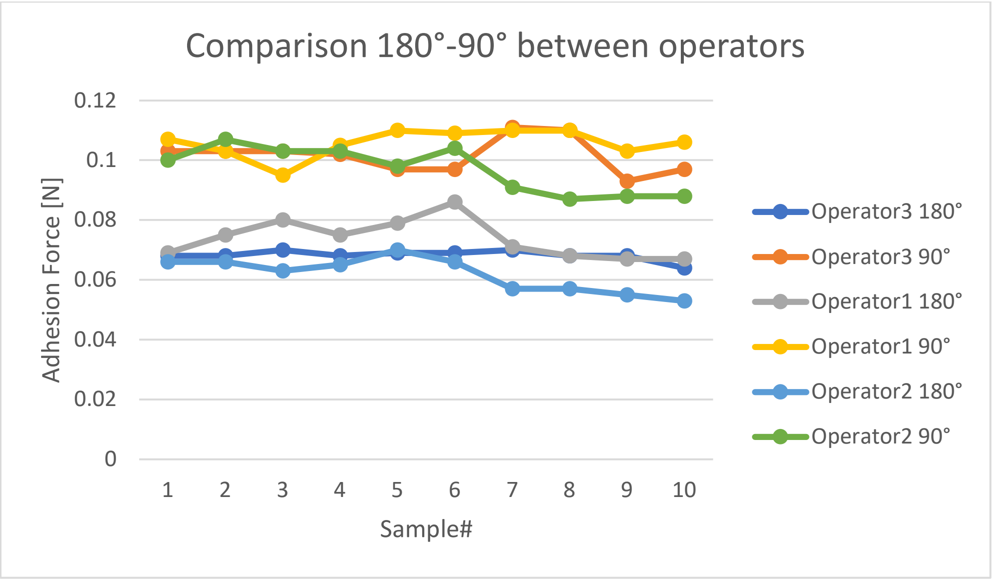


Figura S) Grafico sul confront dei valori ottenuti con I due test. Si nota come i valori del 180 siano superiori.

3.2.6.Confronto dei valori registrati con i tre metodi dai tre operatori

Tabella j. Valori medi dei tre test per i 3 operatori e relativi scarti

	180°Adhesion Force [N]	90° uncoated Adhesion Force [N]	90° coated Adhesion Force [N]	Adhesion F difference 90° coated/uncoated [N]	Adhesion F difference 90°/180° [N]
Op.3					
Avg	0.0682	0.1016	0.3546	0.253	0.0334
Op.1					
Avg	0.0737	0.1058	0.376	0.270	0.0321
Op.2					
Avg	0.0618	0.0969	0.3197	0.2228	0.0351

Osservazioni:

-L’operatore 1 ha i valori più alti per tutti e 3 i test. L’operatore 2 i più bassi. Ci sono due possibili spiegazioni per questo trend:

1. Ogni operatore ha seguito la stessa preparazione del campione; tuttavia, sottili differenze nella preparazione possono influenzare il valore finale registrato. La preparazione dei campioni è l'unica cosa comune ai tre test.
2. Siccome gli operatori hanno testato sempre gli stessi 5 fogli ciascuno e si sono utilizzati 15 diversi batch, la disomogeneità di questi 15 rulli può essere tale da giustificare le differenze di adesione. Questa è l'ipotesi più accreditata, anche considerando che l'operatore 1 per il peel test a 90 coated non era la stessa persona che per gli altri due test, ma ha ottenuto comunque i valori più alti anche in quel caso.

È stata quindi presa la decisione di collezionare i campioni secondo lo studio crossed, quindi i 3 operatori misurano diversi fogli ma tutti provenienti dagli stessi 5 rulli. Però si è deciso di continuare ad utilizzare comunque il programma Nested su Minitab, con l'assunzione che siccome diversi fogli provenienti dallo stesso rullo non sono omogenei (non si può assicurare che abbiano identica adesione), allora possono essere considerati come diversi batch e quindi i batch totali restano 15, potendo pertanto continuare ad utilizzare il programma Nested su Minitab.

3.3.Secondo set di studi MSA

Sono stati quindi impiegati solamente 5 batch, con gli operatori che hanno quindi testato fogli diversi ma provenienti tutti dagli stessi 5 rulli.

A causa di mancanza di tempo è stato possibile effettuare questo studio solo due volte, entrambe per il pull test in direzione z, ma con due nastri differenti (3M e Tesa). Sono stati impiegati i setup che erano risultati migliori durante la fase di sviluppo del metodo (setup1 e 4, rispettivamente).

Il sistema di misurazione, utilizzando il nastro 3M, è risultato accettabile, con una variazione totale pari al 26.82%.

Invece, il sistema di misurazione utilizzando il nastro tesa, è risultato molto lontano dall'essere accettabile, con una variazione totale del 71.79%.

4.Conclusioni

Siccome la "coating adhesion" è un parametro critico da controllare per poter garantire una lunga vita utile alle batterie ioni-litio, vi è necessità di sviluppare uno standard per questa tipologia di test.

In questo progetto, è stato sviluppato un metodo di preparazione dei campioni sia per il test a 90° che per il pull test in direzione z. Successivamente, si è tentata la validazione di entrambi i metodi. Si è quindi cercato di effettuare un paragone tra i test, includendo anche il peel test a 180°, sia a livello statistico, sia a livello pratico, tenendo in considerazione un loro possibile utilizzo all'interno di un laboratorio "production oriented" per il controllo qualità.

Conclusioni dallo sviluppo del metodo:

- Durante la preparazione del campione per il peel test a 90° è necessario andare a rimuovere un lato del coating. Pertanto, gli step risultano identici al peel test a 180° e richiedono molto tempo.
- Secondo l'opinione di molti operatori, il peel test a 90° gradi è più complicato da svolgere. Il grip inferiore ha un peso maggiore e non è semplice da mettere in posizione, il filo è complicato da annodare tra i due grip ed infine è più complesso fissare il foil nel grip superiore.
- Il peel test a 90° registra valori della forza di adesione maggiori rispetto al peel test a 180°. Questo è in accordo con la letteratura che suggeriva una misura più "pulita" a causa di un minore contributo della deformazione del foil per test ad angolazione inferiore.
- Il pull test in direzione z è più semplice e veloce dei due peel test.
- Il principale svantaggio del pull test in direzione z è l'elevato peso dell'intero setup, che è risultato molto difficile per alcuni operatori fissare all'interno del tensile tester.

- Sia i parametri utilizzati sia le tipologie di nastro impiegate influenzano i risultati del pull test in direzione z.

Conclusioni dagli studi MSA

Lo studio nested è stato scelto al posto del crossed perché non si poteva assicurare che diversi fogli, anche dello stesso roll potessero avere la identica forza di adesione del coating.

Utilizzando la prima “versione” dello studio nested, nessun test è stato validato. Si è quindi pensato alle possibili cause di tali fallimenti e si è ipotizzato potesse essere a causa della troppa disomogeneità nell’adesione di 15 diversi rolls. Si è quindi deciso di collezionare i campioni per i futuri MSA dagli stessi 5 rolls per tutti gli operatori. Si è continuato ad utilizzare il programma nested con l’assunzione che anche diversi fogli dello stesso roll non abbiano adesione identica.

Con questo nuovo metodo di collezionare i campioni si è effettuato un nuovo MSA per il pull test con entrambi i nastri e si è riusciti a validare il test utilizzando il “method 2 setup1” per il nastro 3M.

Conclusioni finali

Una volta validato il peel test a 90 potrebbe essere impiegato come ispezione di controllo qualità. Tuttavia, visto che non permette di risparmiare tempo nella preparazione dei campioni e il test risulta essere leggermente più complicato del peel test a 180°, è consigliato utilizzare quest’ultimo.

Il pull test in direzione z è stato validato con successo e potrebbe essere impiegato come ispezione di controllo qualità. Tuttavia, tenendo conto delle considerazioni pratiche, il suggerimento è di preferire il peel test a 180°, almeno fino a quando un sistema più automatizzato del pull test non venga sviluppato. Ad esempio, un sistema che permetta di dover solo preparare il campione e ripulire il grip al termine. Ciò permetterebbe di velocizzare il test che a quel punto risulterebbe più conveniente del peel test.

In generale si può affermare che il peel test vada preferito per un’ispezione più approfondita; l’ausilio del grafico permette di andare ad investigare la presenza di eventuali difetti e ricavarne la posizione di massima. Per un’ispezione più veloce, come un “go/no go” test, che tenga conto solo di un valore limite inferiore, è da preferire il pull test in direzione z.

Lavoro futuro

È suggerito:

- Ripetere lo studio MSA per validare il peel test a 90° utilizzando il nuovo metodo di collezione dei campioni.
- Discutere con il fornitore del tensile tester per sviluppare il pull test semi-automatizzato.
- Trovare una soluzione per pulire i grip dopo il pull test in direzione z.
- Definire un valore limite inferiore per il pull test in direzione z che permetterebbe di ottenere effettivamente un test go/ no go, il che consentirebbe di velocizzare il procedimento di test.

1. Introduction to Lithium-ion batteries

Rechargeable lithium-ion batteries (LIBs) are the current leading energy storage system used in the market of electronic portable devices, such as laptops, smartphones, sensors, etc. in the form of small to medium sized batteries; they are also widely and increasingly used in electric vehicles in the form of large sized batteries. [1] [2] [3] [4]
In fact, LIBs are seen as the most suitable power source as an alternative to fuel vehicles (and more in general to fossil fuels), playing a promising important role in the reduction of carbon footprint, battling against climate change. [2] [5]

LIBs are a crucial part of our daily life. Their application fields and markets have rapidly increased and are showing a continuous rising trend. The market of LIBs, was estimated at 41.1 billion $ in 2021 with a future increase of 12.3% up to 2030, according to Gonçalves et al. [1] [6]

The widespread use of LIBs is mainly due to their superior properties in comparison with other batteries, such as lightweight, low cost, high energy and power density, no memory effect, long lifetime and high number of charge/discharge cycles. [1] [4] [6] [7]
They also have a high energy conversion rate, allowing them to be used also as energy storage systems for renewable sources such as wind, solar and geothermal. [5]

Many efforts have already been made to improve the power level of LIBs, as there is a persistent demand for higher energy densities. Therefore, research in this field is increasing more and more. Between 2017 and 2019, more than 53’000 articles presenting research results on LIBs were published. [8] [9]

1.1 Components and operation

LIBs convert chemical energy into electrical energy through electrochemical reactions. Figure 1.1 shows the typical main components of a LIB: anode (negative electrode, usually a form of carbon such as graphite), cathode (positive electrode), separator and electrolyte. [5]

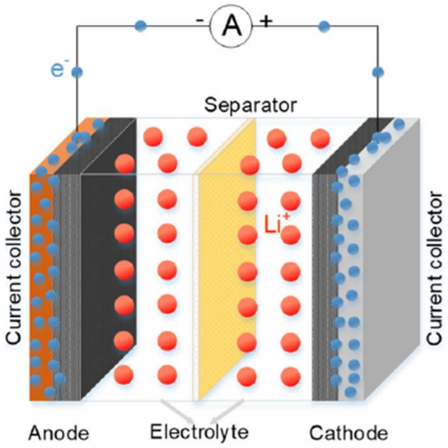
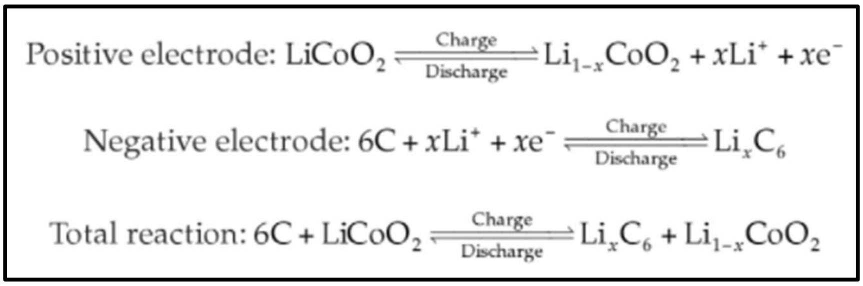


Figure 1.1 Main components of a LIB [5]

LIBs generally operate on the principle of reversible intercalation of positively charged lithium ions (Li+) in the cathode and anode. In the discharged state, lithium (Li) atoms are only contained in the cathode. On charging (applying a current that provides electrons to the anode), Li+ ions are deintercalated from the layered cathode, transferred through the electrolyte as a medium and across the separator, to be intercalated between the graphite layers on the anode side. On discharge the reverse process occurs where the electrons pass through the external circuit to power various systems. [10] [11] [12]

The charge and discharge process can be explained by the following reactions (fig.1.2), considering lithium cobalt oxide ($LiCoO_2$) and graphite as electrode materials, cathode and anode respectively. The nature of the electrochemical reactions depends on the chemistry of the electrodes. [13]



$$\text{Positive electrode: } LiCoO_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + xLi^+ + xe^-$$

$$\text{Negative electrode: } 6C + xLi^+ + xe^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_xC_6$$

$$\text{Total reaction: } 6C + LiCoO_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_xC_6 + Li_{1-x}CoO_2$$

Figure1.2 LIBs reactions [13]

The electrolyte enables the flow of Li+ ions between the electrodes. Most common electrolytes include a salt, which is usually lithium hexafluorophosphate ($LiPF_6$), which is dissolved in a mixture of solvents, usually dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC). [14] [15]

The separator is usually a microporous membrane made of polyolefin. Its function is to prevent a direct contact between the anode and the cathode (that's why it is placed in between them) and no flow of electrons, while enabling Li+ ions to pass through. In fact, the separator isolates the electrodes and electric contacts to enable electron transport via an external circuit only. Polyolefins provide only limited heat resistance, therefore research is also focusing on other materials such as silicon rubber, aromatic polyamide resin, liquid crystalline polyester resin, to name a few. A separator should provide not only high temperature stability and safety, but also excellent ion transportation. [10]

1.2 Types of cells

There are three main types of battery cells:

- Prismatic: used for LIBs in the industrial sector and in the automotive industry to produce medium to large battery modules and packs. [16]

Figure.1.3 Image of prismatic cells [17]

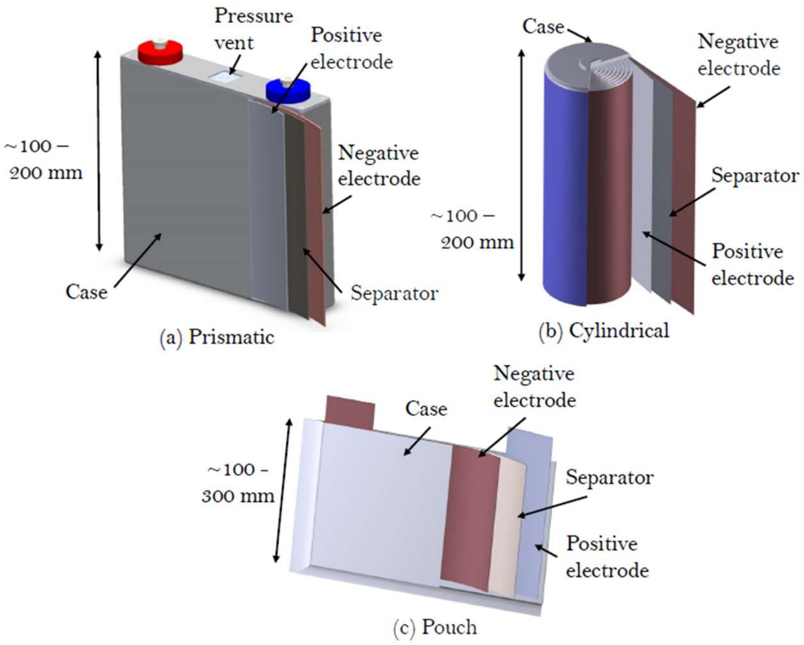
- Cylindrical cells: normally used in small LIBs (<2kWh), for example, electric bikes, screwdrivers, etc. [16]

Figure 1.4 Image of cylindrical cells [17]

- Pouch: used especially in high-power applications (high voltage and low capacities) or in applications where a reduction in volume is required, for example, electric vehicles.

Figure 1.5 Image of pouch cells [16]

Essentially, they all consist of a jelly roll[1] and a container, the differences are in the stiffness of the container and the assembly of the jellyroll.
For pouch and prismatic cells this is obtained by stacking electrodes and separators layer by layer. For the cylindrical cells, instead, the jelly rolls are constructed by winding the layers to obtain a cylindrical configuration. [18]



(a) Prismatic

(b) Cylindrical

(c) Pouch

Figure 1.6 A schematic representation of the assembly of the three cell types [19]

---

[1] Finished stack or winded roll; design of a cell (anode, separator and cathode layered one on the other).

2. Battery manufacturing

The battery manufacturing process includes three major processes: the electrode manufacturing, the cell assembly and the formation and aging and end of line process. [6] [20] [21]

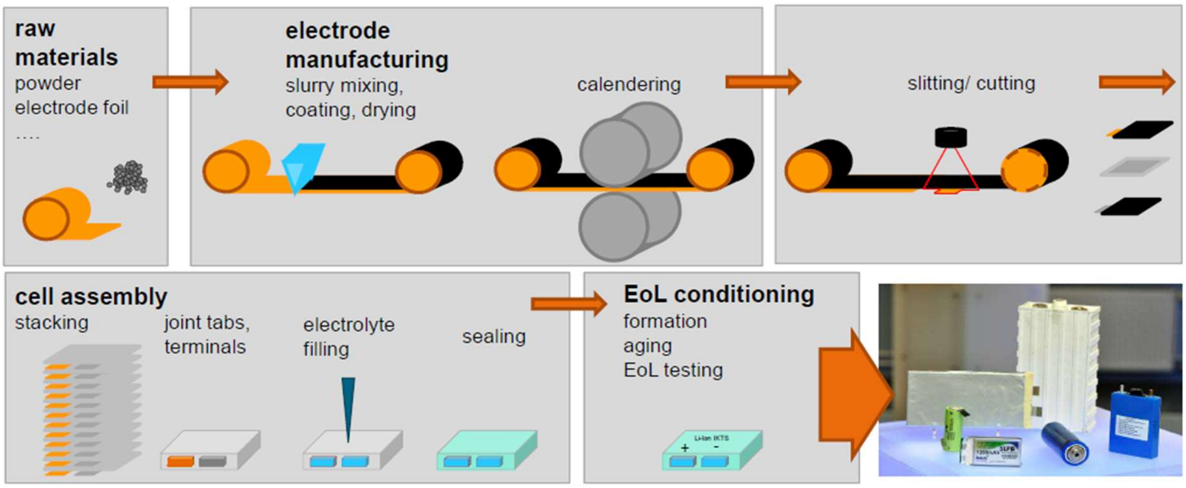


Figure 2.1 Schematic overview of the battery manufacturing process. [22]

As the experiments for this thesis project are going to be performed on calendered coated foils the following section will mainly focus on the electrode manufacturing process, in order for the reader to better understand the process parameters that can affect the adhesion strength of the interface between the current collector foil and the coating of the electrodes that are going to be investigated.

2.1 Electrode manufacturing

The electrode manufacturing process includes several different steps: mixing, coating, drying and solvent recovery, calendering, slitting and vacuum drying. All the steps from calendering are performed in a clean and dry room. [6] The most important steps, with regards to the project of this thesis, being the coating, drying and calendering steps, which are the ones on which this literature review is mainly focused on.

2.1.1 Mixing

Mixing can be divided in two further steps: mixing (dry) and dispersing (wet). In the mixing step the active material (AM), usually graphite for the anode and a lithium nickel manganese cobalt oxide (Li-NMC) for the cathode, a conductive additive (e.g. carbon black) and a binder are mixed. In the dispersing step a solvent is added to obtain a disperse and homogeneous slurry. Planetary mixers are usually used to prepare slurries in an industrial production setting. Different solvents are used for cathode and anode: usually N-methyl pyrrolidone (NMP) is used for the cathode to disperse the binder which is usually polyvinylidene fluoride (PVDF). Whilst for the anode, styrene-butadiene rubber (SBR, additive) with carboxymethyl cellulose (CMC, binder) are dispersed in deionized water (solvent). The role of the binder is to prevent formation of cracks improving adhesion and elasticity of the coating. Mixing conditions and operations can affect the electrochemical performance of the electrodes. [6] [20]

2.1.2 Coating

The slurry is then deposited on a metallic foil acting as a current collector (usually copper (Cu) for anode and aluminium (Al) for cathode), typically through a slot die, to obtain a uniform coating. The coated foil is transferred to the dryer, and then back to the coating system to be also coated on the other side of the foil, so that eventually both sides of the foil are coated with the electrode slurry. [6] [20]

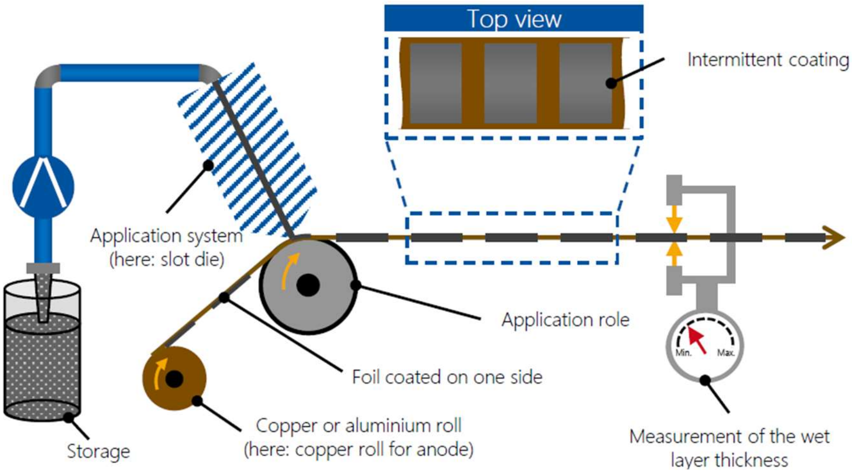


Figure 2.2 Scheme of a foil coating system [20]

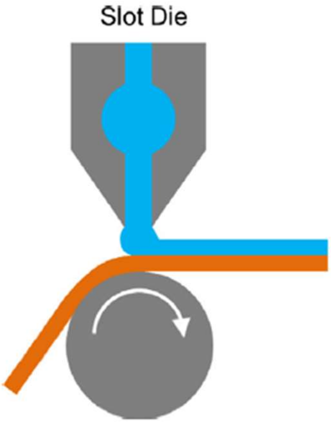


Figure2.3 Illustration of the slot die [23]

The coating process can be achieved in different ways. For big industries, the reel to reel coater is the most used common equipped used. Several parameters of the coating are key to monitor the quality of the coating. These are the thickness, the coating loading weight and any presence of defects on the coating. The properties of the coating are mainly affected by the slurry recipe and the mixing parameters and therefore mainly by the properties of the slurry. In particular, the thickness is a very important parameter, as thicker coatings contain a higher quantity of active material resulting in higher energy densities and greater diffusion distances, but may cause quicker degradations. Hence, it is important to stay in the optimal range of thickness that can balance these effects. [23] [24]

There are different ways to measure and monitor the thickness. One way that allows 100% automatic monitoring (with no need to stop the coating process) is using laser position sensors. The coating loading weight is related to the thickness, therefore only one of the two parameters is usually measured.
The presence of defects also affects the performance and safety of LIBs. There are three main possibilities to detect defects: visual inspection, IR thermography and optical imaging. [23]

Many different studies have been performed on the coating binder content and distribution. One of these has compared different possible configurations with different binder compositions and distributions. Figure 2.4 represents a cross section of the multilayer stacks and the percentage of binder content in the layer closest to the current collector foil (bottom layer), and a second additional layer (the top layer). Table 2.1 shows the different compositions of each of the slurries used for each layer. [25]

Figure 2.4 Cross-section of the multilayer stacks and percentage of binder content in each layer [25]

Table 2.1 Composition of the slurries used for each layer [25]

ID	Graphite [wt%]	CB [wt%]	CMC [wt%]	SBR [wt%]	Solids [wt%]
C2	96.60	1.45	1.95	0	43.9
B2	94.20	1.42	1.89	2.49	43.3
A	93.00	1.40	1.87	3.73	43.0
B1	91.80	1.38	1.85	4.97	42.7
C1	89.40	1.34	1.80	7.46	42.2

The (correct) assumption was that the adhesive force between the coating and the current collector foil is mainly determined by the distribution and content of SBR binder in the position closest to the current collector foil. In fact, results have shown that by doubling for example the SBR binder content directly on the current collector, the adhesive force also increases to approximately twice the amount (23.0 in A only to 44.0 in C1 only). This is a very important conclusion because multilayered electrodes with different SBR binder content and distribution in the lower layer can lead to a significant reduction in the total binder content without any negative impact on adhesion. Fig.2.5 shows the adhesion strength of the different configurations. [25]

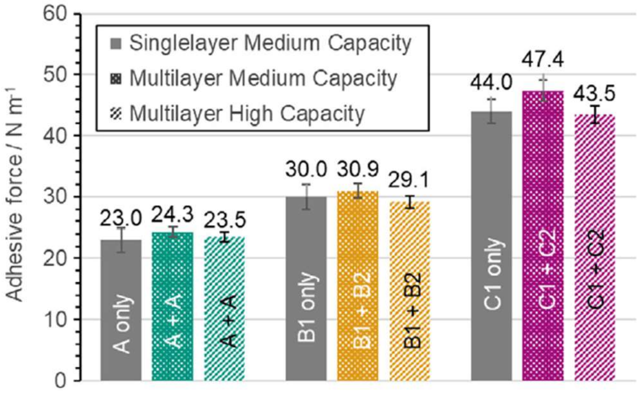


Figure 2.5 Different binder content and distribution configurations with the relative value of adhesion force

The best multilayer configuration is the C1+C2 configuration, because it has the highest adhesion strength with the same total SBR content as A+A and B1+B2. [25]

Another study showed a similar conclusion. The adhesion of an anode with low binder content (1%) and high binder content (3.7%) was investigated; a third configuration was investigated and can be seen in fig2.6. A thin primer layer (bottom layer) with a very high binder content was placed at the interface with the foil, while the top layer, called active layer had the binder content of the first "low binder anode" (1%). Tab2.2 shows the composition used for the slurries. [26]

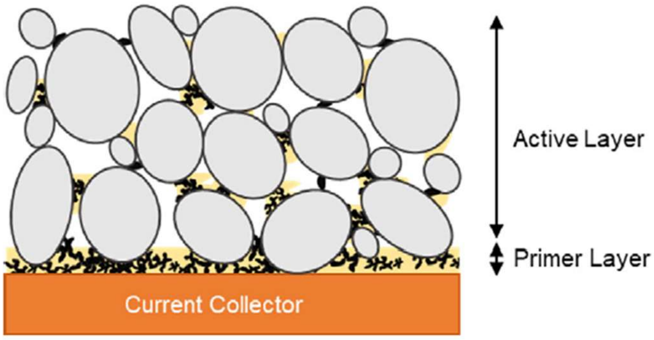
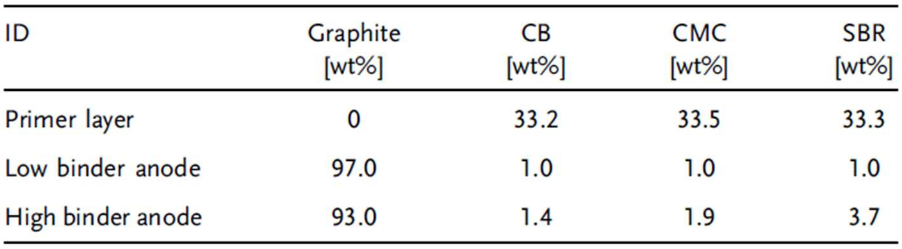


Figure 2.6 Representation of the different layers [26]

Table 2.2 Binder content in the different configurations [26]



ID	Graphite [wt%]	CB [wt%]	CMC [wt%]	SBR [wt%]
Primer layer	0	33.2	33.5	33.3
Low binder anode	97.0	1.0	1.0	1.0
High binder anode	93.0	1.4	1.9	3.7

The adhesion of the anode with low binder content is 1.5 N/m, as shown by fig.2.7. As expected, this is much lower than the 9.7 N/m of the anode with high binder content. By using the primer layer, the adhesion is increased from 1.5 to 8.1 N/m. The electrodes with primer can therefore be processed similarly to the electrodes with high binder content. The addition of a primer layer reduces the proportion of active material in the electrode from 97.0 to 96.5 wt%; this is a very small loss of energy density in relation to the achieved improvement of adhesion. [26]

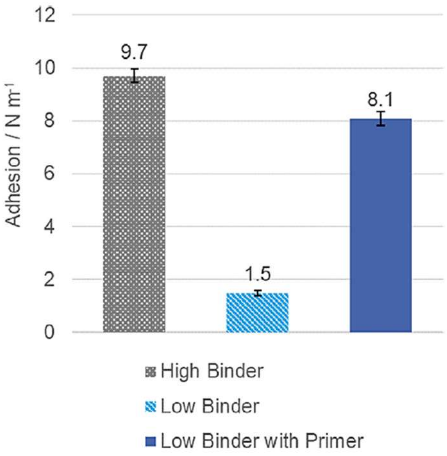


Figure 2.7 Adhesion with different binder content

It has also been demonstrated that CMC does not contribute to the adhesive strength of LIB anode layers. It is therefore fundamental to add SBR which lead to a consistent increase of adhesion at the interface. [27]

2.1.3 Drying

After coating, there is a continuous drying step, to evaporate the solvent, which is recovered or used for thermal recycling. The transport of the foil can be realized by a roller system or by a flotation system. The latter one is used for a simultaneous double-sided coating. In most cases, however, the coated foil must pass twice in the dryer to obtain drying of both sides. [6] [20]

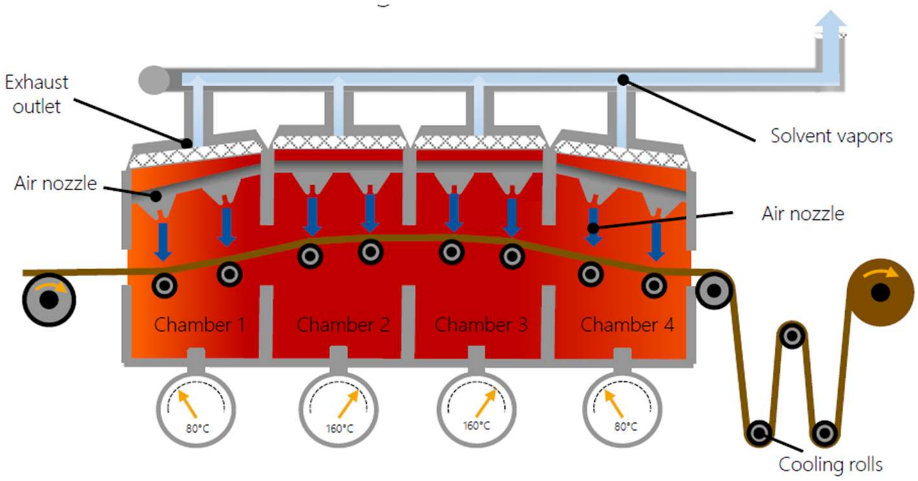


Figure 2.8 Schematic representation of the drying process [20]

The drying process is a crucial step for the adhesion strength of the coating to the current collector. The parameters to be monitored in this step are temperature (T) and drying velocity. The latter one in particular affects the adhesion because it can cause the binder to migrate away from the interface with the foil, resulting eventually in a poor adhesion strength of the coating to the foil, which ultimately causes delaminations and early capacity fades and decreasing battery cell performance.

This has been shown for example by Kumberg et al. [28] They demonstrated that when drying at two different drying rates at identical isothermal drying temperature, the adhesion is worse for electrodes dried at higher drying rates. In fact, above a certain drying rate, almost no SBR binder remains at the interface between active material and current collector. [28]

The reason why the binder is accumulated at the film surface during drying, is to be found in capillary transport which is the main initiator. Thick electrodes partly dry by solvent diffusion through the microstructure, but their main drying mechanism is capillary transport, dragging the binder to the surface. In fact, additives within the solvent are dragged to the film surface along with the solvent, where they are left behind as the solvent evaporates. [28]

Higher temperatures might be beneficial for binder mobility, compensating its accumulation at the surface to some extent, compared with drying at the same drying rate but at a lower temperature. [28]

2.1.4 Calendering

Calendering is performed by compressing the dried coated foil on both sides through a rotating pair of rollers. This step allows to optimize some physical properties of the electrode such as porosity, bonding (improves particle contact, cohesion and coating adhesion), density and conductivity. In particular, the strength applied by the two rollers generates a line pressure that affects some of the aforementioned properties, especially the porosity of the coated material. A decrease in porosity maximizes particle contact and leads to an improvement of the energy density of the cell, leading to an improvement of the electrochemical properties. There is an optimal range of values of the line pressure in order to leave sufficient porosity for lithium transport If the pressure is too high it may generate cracks in the coating, affecting the performance of the cell. If it is too low, an effective reduction in porosity may not be achieved. [3] [6] [20] [23]

During calendering the parameters that affect the binder and the adhesion strength are mainly compression rate, diameter of the roll and temperature of the process. [29] [30]

The main drawback of calendering is the fact that compression might lead to a lateral expansion of the coating, resulting in a reduction of coating adhesion. In fact, due to different expansion properties, the coating has a more pronounced longitudinal and transverse expansion compared to the current collector, leading to the formation of shear stresses at the interface (only the coating is in contact with the rolls). That is why it is so important to remain in the optimal line pressure range, avoiding this side effect. Temperature has also an important role in avoiding this effect. It has been proven by Billot et al. that adhesion is improved at high roller temperatures thanks to recrystallization of the binder. For example, heating at 165 °C, just below the melting temperature of PVdF and cooling slowly, allows recrystallization and stress reduction. In fact, the shear modulus of the PVdF binder decreases linearly with increasing the temperature and the loss factor assumes higher values. Therefore, the binder approaches an ideal viscous behaviour. Moreover, this binder has a low glass transition temperature (-35 °C); this makes it easier for the binder to rearrange itself in the pores at higher temperatures, contributing to a better crosslinking of the particles among each other and to the substrate during cooling. The effect of annealing is greater as temperature gets closer to the melting point of the binder. [30]

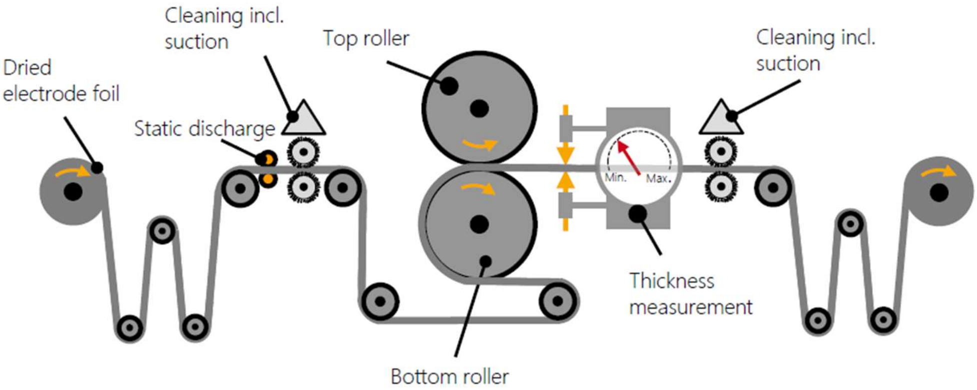


Figure 2.9 Example of the calendering step [20]

2.1.5 Slitting

Slitting is performed with a machine that uses a blade or a chisel or the so-called rolling knives that cut the main coil into many different smaller electrode coils, in order to obtain the final dimensions of the cell. The cutting width depends on the cell design and varies according to it. [6] [20]

2.1.6 Vacuum drying

In the end, vacuum drying is performed to remove residual solvents and reduce the excess of water to lower the moisture level and minimize risk of corrosion and other side reactions that could lead to safety issues. For this purpose, an inert gas might be used in the vacuum ovens. The reduction of moisture is obtained by evaporation, operating at low temperature and low global pressure. It is a necessary step that has to be done, even if it is quite expensive in terms of energy and time (12-30h). When the vacuum drying is completed, the coils are transferred directly to the next step in the process. [6] [20]

2.2 Cell assembly

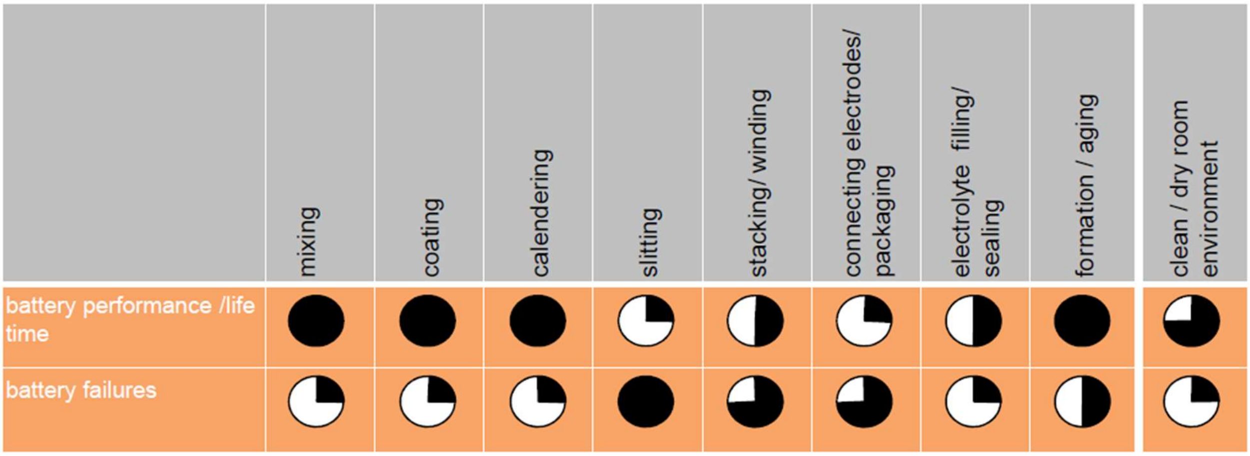
After the electrode manufacturing process, follows the cell assembly process. This process can be divided in the following steps steps: separation, stacking, packaging, electrolyte filling and winding. [20]

2.3 Formation, aging and end of line

The final process in battery manufacturing is the formation and aging and end of line process; it is divided in the following steps: roll pressing (optional), formation, degassing, aging and end of line (EOL), packaging and shipping. [20]

2.4 Conclusions on battery manufacturing

The following diagram in fig. 2.10, created by Wolter et al, shows the relevance of process steps regarding battery quality.



	mixing	coating	calendering	slitting	stacking/ winding	connecting electrodes/ packaging	electrolyte filling/ sealing	formation / aging	clean / dry room environment
battery performance /life time	●	●	●	◔	◑	◔	◑	●	◕
battery failures	◔	◔	◔	●	◕	◕	◔	◑	◔

Figure 2.10 Relevance of process steps in battery quality [22]

We can assume that Mixing, coating and calendering (three steps of the electrode manufacturing), along with formation and aging are the steps that mainly influence the performance/lifetime of the battery cell. While battery failures are mainly caused by the slitting process.

3. Coating adhesion

The adhesion strength is defined as the maximum force that has to be applied to separate a coating from a substrate. In the case of LIBs electrodes, the substrate is the metallic foil, either Al for the cathode or Cu for the anode, as seen in the previous chapter. [31]

3.1 Why is coating adhesion important?

Coating adhesion strength of LIBs electrodes is a very important mechanical property as it affects the electrochemical lifetime, cycle performance and stability of battery cells.

Coatings have to withstand further process steps, mentioned in the previous chapter, such as electrode slitting, winding and electrolyte filling, among the others. The coatings must obviously also resist mechanically once the battery manufacturing process is finished, in fact mechanical resistance is required during cell operations. [31]

Lithium intercalation and de-intercalation (charging and discharging cycle) causes volume expansion and shrinkage of the active material particles, inducing the formation of mechanical stresses. The swelling leads, in fact, to the formation of mechanical tensions at the particle-binder interface leading to the formation of cracks, or local delamination of the coating from the current collector. This compromises the electrical contact, causing inhomogeneities in current density and decreasing cycle stability. This is why the adhesion strength of the coating affects lifetime and performance of LIBs. [27] [30] [31] [32] [33] [34]

Silicon has been intensively studied and is considered as a possible future material for anode, replacing graphite as active material thanks to its high theoretical specific capacity: 4’212 mAh/g ($Li_{22}Si_5$), which is ten times greater than the specific capacity of graphite (LiC_6, 372 mAh/g). The problem is that its volume expansion is much higher (up to 300%), possibly causing delamination of the electrode layer from the current collector that can then result in a loss of electrical conductivity, the continuous growth of the solid electrolyte interphase (SEI), and capacity fade. [30] [35] [36]

Among all the process factors mentioned in chapter 2, the composition (binder amount and distribution in particular), coating thickness and the parameters involving the drying and calendering steps (drying T, drying rate, final porosity, pressing T etc.), are the ones that mainly affect adhesion strength. A good adhesion strength avoids delamination of the coating also during cell assembly and other steps in the battery manufacturing process, as well as once the battery cell is in operation. In order to have an improved adhesion strength, an idea could be to increase the amount of binder, but this could lead to the use of a lower amount of active material, reducing the final energy density of a cell. Therefore, it is important to balance the two properties with a most suitable amount of binder and AM. [30]

3.2 How to measure coating adhesion of electrodes?

An ideal adhesion test method measures only the coating adhesion, but other properties of coating, substrate or interface usually affect the results in every well-known test method. [37]

There are many different tests that can be used to measure the adhesion strength of the coating bonded to the current collector. Examples are:

- 180° peel test
- 90° peel test
- Z-direction pull test (also known as pull-off test)
- T-peel test.

To perform all these tests a universal testing machine (tensile tester) is needed.

The adhesion strength is defined as the maximum force that has to be applied to separate a coating from the substrate. In terms of equations, adhesion strength can be defined as:

$$\sigma = F_f / A \qquad Eq.3.1$$

where F_f is the magnitude of the peak axial force, A is the area of the failure interface of the electrode. The stress distribution is assumed to be uniform across the failure interface. [38]

According to Gaikwad et al. on a study performed in 2017, there were no standard protocols to measure the adhesion (and cohesion) strength of battery electrodes, and up to now a standard has not been developed yet. [34]

3.2.1 Failure modes during adhesion testing

Batteries can rapidly loose capacity and decrease their lifetime if a delamination of active layers (interface between the coating and the current collector) and/or a loss of particle-to-particle contact within the coating takes place. [34] Hence, it is important that the adhesion testing setup mimics/measures as close as possible the real possible failure mode occurring at those interfaces within a battery cell.

In the multi-layered arrangement during an adhesion test, three locations are critical, where fracture/failure might occur:

a) Adhesive failure at the coating-substrate interface (where the substrate is the current collector)
b) Cohesive failure inside the coating itself
c) Adhesive failure at the coating-substrate interface (where in this case the substrate is the tape). This specific failure defines the measurement limit

Failures a) and b) are the one that are expected to happen when delamination occurs during the service of the battery. Although, it is unclear to which extent and which one is the most dominant. Failure c) instead, happens during test adhesion as it involves only the tape; it is something to be aware of, choosing a tape strong enough to avoid this failure.

Fig 3.1 illustrates the three cases that can be observed (during a pull-off test for example). Specifically for the pull-off test, Haselrieder et al. have performed several tests, observing only adhesive failure (between current collector and coating). [31]

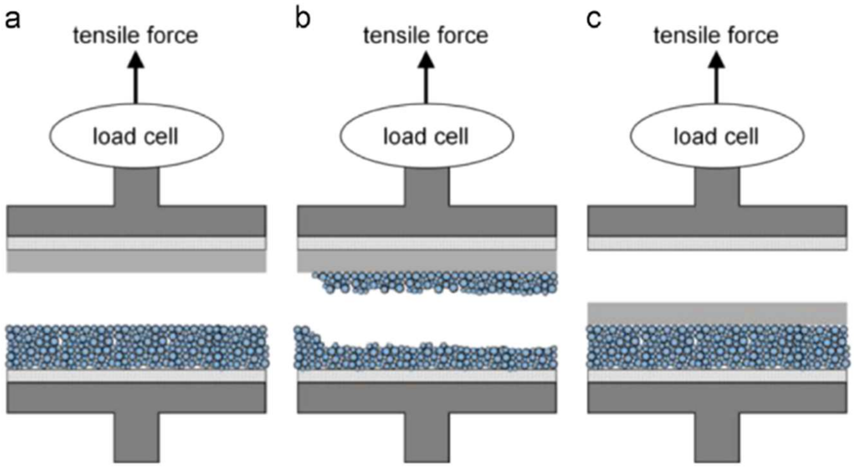


Figure 3.1 Representation of the three failure modes observed during a Pull-off test [31]

Failures that happen at a) and b) are named “adhesive failure” and “cohesive failure”, respectively. In fact, a failure of adhesive joints is commonly said to be adhesive or cohesive (a combination of the two is also possible). An adhesive failure occurs between the interface of an adhesive and an adherent and it is the most common scenario (de-bonding between coating and current collector), according to Luo et al. It is said to be dominant when the degree of removal (DoR) is at least 0.95. [31] [38] [39]

Combined tensile and shear tests using dog bone specimens were performed by Luo et al. [38], at 0°, 45° and 90° to investigate the possible failure modes of electrodes. For 0° the dominant failure mode is cohesion failure, while for 90°, adhesive failure is the dominant failure mode, with just a few particles remaining bonded to the current collector. In fact, it was observed that from 0° to 90° the percentage of adhesive failure increases. [38]

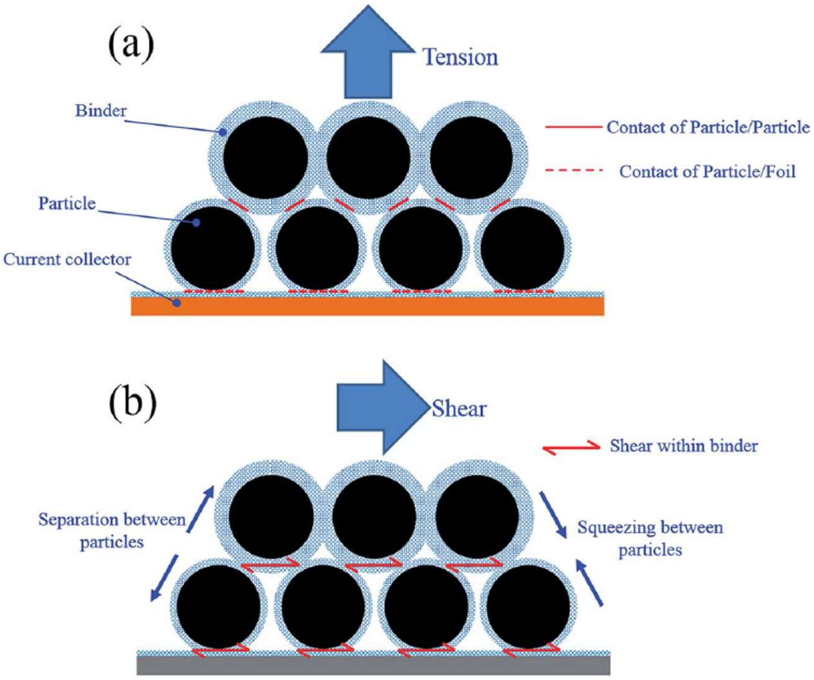


Figure 3.2 Representation of failure mechanism under tension (a) and shear (b) [38]

3.2.2 Tensile tester

A tensile tester, also known as pull tester or universal testing machine (UTM), is an electrochemical (or hydraulic) test system that applies a tensile force on a material to establish its tensile strength. [40]

The difference between electrochemical and hydraulic is the method by which the load is applied; in the electrochemical ones it is based on a variable speed electric motor, while the hydraulic ones use either a single- or dual-acting piston to move the crosshead up or down. [41]

Tensile strength can be defined as the force per unit area to fracture the specimen, or the highest value of engineering stress (s, nominal stress) which is defined as:

$$s = F/A_0 \qquad Eq.3.2$$

[41]

where F is the tensile force, and A_0 the initial cross-sectional area of the gage section.

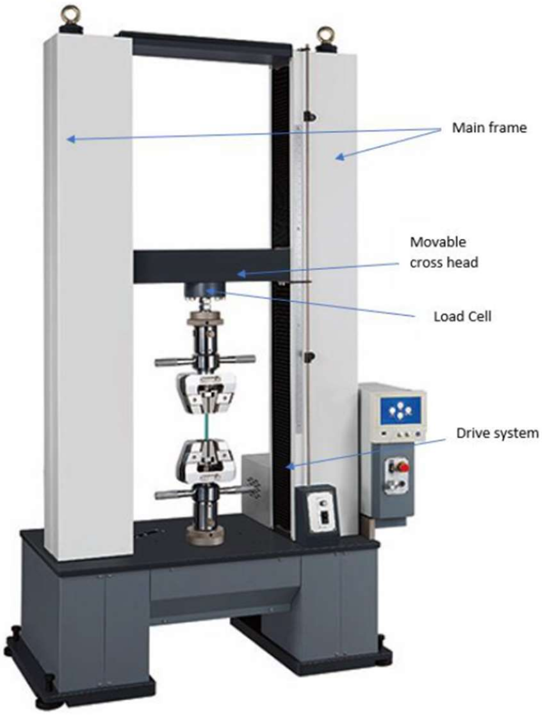


Figure 3.3 Photo of a tensile tester [42]

A universal testing machine (UTM) is mainly composed of six parts:

- main frame
- load cell: located in the upper side of the frame, is used for both tensile and compression test.
- movable crosshead
- drive system: includes a stepper motor with adjustable velocity
- two grips: used to clamp the specimen firmly, avoiding slippage during test. One is placed on the load cell, and the other on the movable crosshead.
- digital indicator: records the crosshead displacement [43] [44]

The machine is controlled by a setting software. Throughout the test the force applied and the elongation (or displacement, depending on the test) of the specimen are recorded. [40]

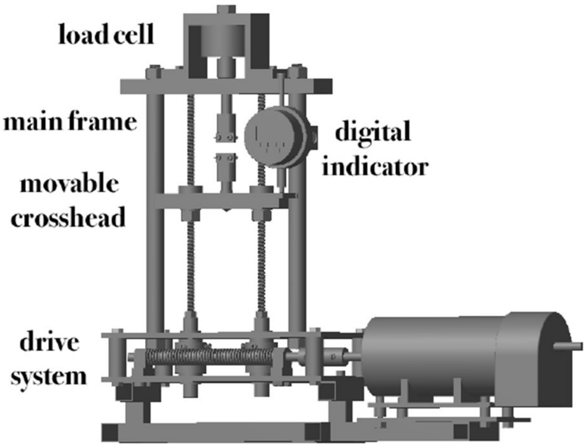


Figure 3.4 Representation of a UTM [43]

3.2.3 The peel test

A peel test is usually performed to measure the adhesion strength of joints; there are many types of peel tests. The climbing drum peel test, for example, is used for sandwich structures in the aerospace industry. [45] The T-peel test and the 180° peel test, have widely been used in the aeronautical industry to measure the peel strength of metallic joints. [46] The decision on which type of peel test to use depends on the types of adhesives, types of materials that are joint, and the flexibility of these materials. [39]

The peel test is one of the most used tests in the battery industry to measure the coating adhesion strength of electrodes and control the adhesion quality. The test can be performed at various angles from 0° to 180°, but the most used ones in the battery industry are the 90° and the 180°. These tests are performed using commercial double-sided adhesive tape and a universal testing machine (UTM). [47] A piece of adhesive tape is applied on the coating of the electrode that has to be tested and is then removed through the UTM in order to obtain the peeling strength. During the test, the interfacial cracks propagate in a stable manner, and the final curve that is obtained shows the force versus the displacement. [48]

More in detail, the tape is firmly pressed on the coating to avoid the formation of air bubbles. The coating is (in some cases) removed from the electrode's opposite side of where the tape is stuck, and the foil is partially detached from the coating and clamped to the grip of the movable crosshead of the instrument which moves upwards and peels off the foil from the coating, allowing to record the adhesion strength. In fact, the load cell measures the force required to remove the coating from the substrate (peeling force). The adhesion strength of the electrodes can be expressed in terms of the force per unit width of the tape (N/mm) at a constant speed. [34] [39]

$$Peel\ strength\ (N/mm)\ = \frac{\text{Peeling Force (N)}}{\text{Specimen Width (mm)}} \qquad \textit{Eq.3.3}$$

The adhesion strength is affected by peel parameters, such as peeling rate and peeling angle, and by measurement conditions, for example type of adhesive tape, adhesion status between tape and sample surface, time of adhesion, temperature, humidity, sensitivity of the test machine, etc. [39] [47]

The value of the adhesion strength should be characteristic of the joint and ideally independent from geometric parameters. The adhesion strength usually also includes a contribution from plastic and viscoelastic energy dissipation. This occurs locally at the crack tip, and it is a function of the rate at which the peel test is performed. This additional contribution to the peel force decreases with increased peeling rate, according to Gent et al., but high rates might give unsteady peeling. [39] [49] [50] [51]

In fact, the main problem of the peel test is that the force applied not only separates the coating from the substrate, but also contributes to a plastic deformation. So, it is important to evaluate both effects to record the effective adhesion strength of the coating, and this is an important challenge. In fact, the determination of the adhesion strength from the total energy (G, also called work of detachment) to generate a peel fracture, is a classical problem in the Peel test. [48] [49]

The additional contribution towards work of detachment (energy,) that arises from bending the adhering layer from the substrate, is going to be bigger at larger peeling angles as the adhering surface is going to be more bent. For inextensible layers, there is a good approximation of the work of detachment G according to:

$$\mathrm{G} = \mathrm{P}\ (1 - \cos\theta) \qquad \textit{Eq.3.4}$$

where P is the peel force and θ is the peeling angle. The shortcoming is that deviations from this theoretical dependence are almost always present. [52]

The influence of peel angle has given contradictory results according to Sugizaki et al. At low angles, the theoretical dependence is not followed, but, in general, the work of detachment was found to be higher for the 180° than for the 90 °. [50]
In fact, the contribution of plastic yielding towards the work of detachment is much lower for the 90° peel test than for the 180° peel test, and this is why the 90° peel test is considered a "cleaner" measure. [51]

The main advantages of the peel test are minimal cost, simplicity and controllable crack propagation. It can also be used to investigate the effect of inhomogeneity of the coating while measuring the adhesion and can allow the study of adhesion as a function of interfacial crack position. [48]

The following figure (3.5) shows a typical peel force curve. The X axis is the peel length, usually expressed in mm. The Y axis is the force, usually expressed in N.

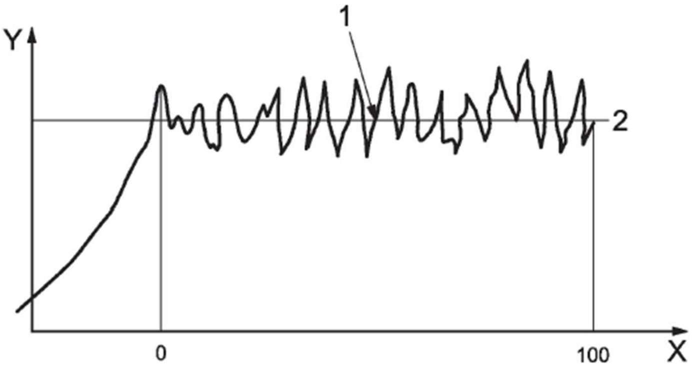


Figure 3.5 Typical peel force curve obtained after a peel test [53]

The 90° peel test

In this test, the double-sided tape is used to stick the electrode to a rigid plate that is clamped to the lower grip. The foil is then manually partially peeled and clamped in the upper grip that is going to move upwards and peel off the foil from the coating at a constant rate, in such a way that separation occurs progressively along the length of the interface foil coating. The force is applied approximately normal to the plane of the bond, and in order to maintain the angle at 90 degrees, the lower fixture, that includes the grip in which the plate is clamped, moves sidewards at a constant speed as the foil is peeled off, thanks to a wire that has to be placed by the operator. The wire has to be tightened on one end with a knot to the lower fixture of the test setup, and the second end is tightened to the tensile tester rolling it a couple of times around a special dial knob. A mandrel can also be used to maintain the angle while peeling, as shown in fig3.6. In both cases the adherend must be flexible, to have a uniform pulling and so that the angle is maintained at 90°. [39]
This test is commonly used when the upper adherend is flexible and the lower is rigid, but using the rigid plate allows to have both adherends flexible. [39]

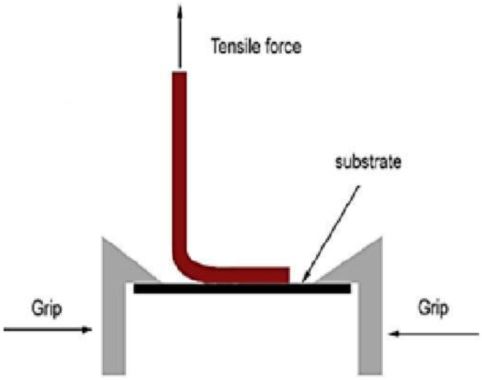


Figure 3.6 Representation of the 90° peel test without mandrel. [39]

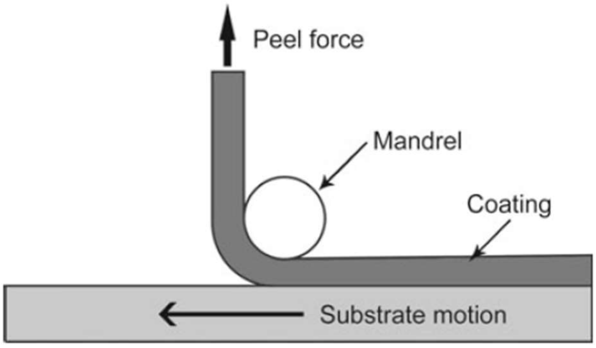


Figure 3.7 Schematic representation of the 90° Peel Test using a mandrel. [48]

As mentioned, the 90° peel test gives a "cleaner" measurement compared to the 180°. Nevertheless, one of its shortcomings is that it is more difficult for the operator to clamp the plate to the movable lower grip and the foil to the upper grip, needing more time than for the 180° setup.

The 180° peel test

In the 180° eel test, same as for the 90° peel test, the sample is stuck to an aluminium plate with the help of to a double-sided tape. This plate is then clamped in a vertical position, as shown in fig. 3.8. The foil is then manually partially detached from the coating and clamped to the upper grip that moves upwards and peels off the foil from the coating. The material that has to be peeled (the foil in the case of the electrode) must be sufficiently flexible to be bent back by 180° and clamped to the grip, so that there is a uniform bending while the pulling action is performed. This test seems to be favoured for non-structural adhesives such as tapes and pressure sensitive adhesives. [45] [39] [54]

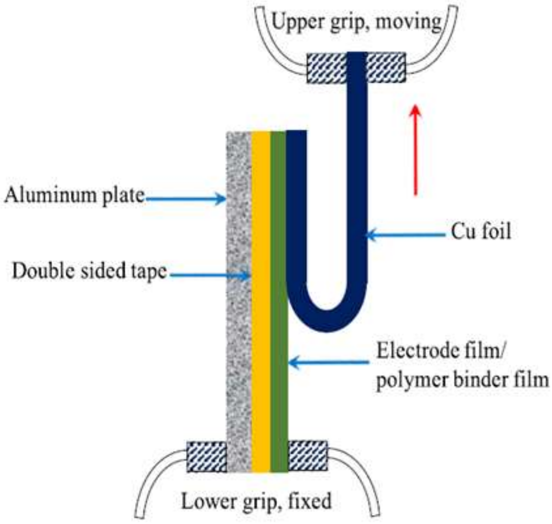


Figure 3.8 Schematic representation of the 180° Peel test performed on an anode specimen [35]

The T-peel test

The T-peel test is a type of peel test, in which both materials are peeled simultaneously at a constant separation speed using a UTM. One end of the joint is clamped in the first grip, while the other end is clamped in the second grip which moves upwards allowing the peeling. This type of test can only be used when both adherends are flexible, in order to obtain a uniform bending and peeling. [45] [39]

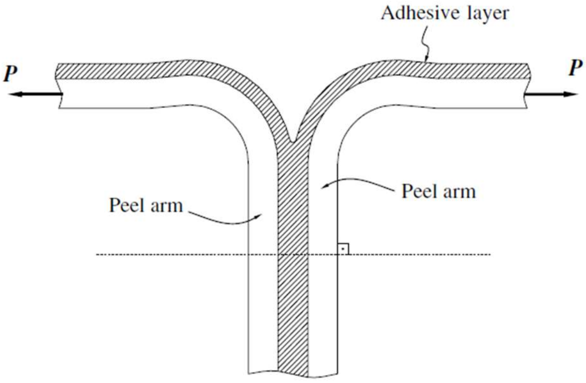


Fig. 2. The T-peel test.

Figure 3.9 Schematic representation of a T-peel test [49]

The T-peel test depends on the geometry and the materials of the joint. The parameters that mainly affect the test are thickness, stiffness and plastic yield strength of the adherend material. Most of the deformation during the test occurs in the adherend, which affects its stress distribution. In fact, the amount of flexibility of the adhesive can alter the location of the stress maximum. [45]

The T-peel test is widely used to evaluate surface treatments and the environmental durability of adhesives. [54]

3.2.4 The z-direction pull test

The adhesion between the coating and the metallic foil may also be measured using a z-direction pull test, also known as a pull-off test. [35]

The principle at the base of this measure is shown in fig. 3.10. The electrode that has to be tested is placed between two plane parallel plates (also called grips), using a double-sided adhesive tape. A compressive force is then applied to obtain an adhesive bond between the adhesive tape and the electrode. A 'pull-off' is then performed in which the opposite planar base moves upwards with high (but defined) speed. The maximum tensile force is then recorded at the point of adhesive failure as the characteristic value by a load cell. [31]

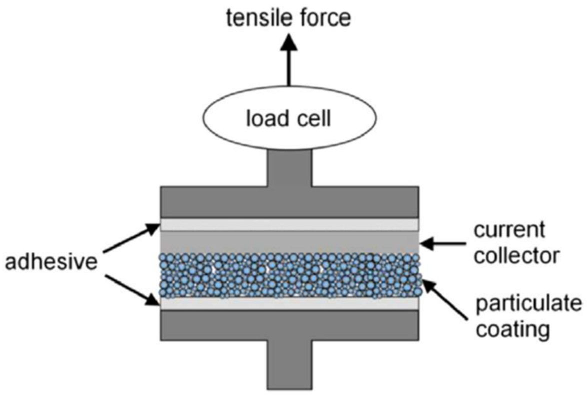


Figure 3.10 Pull-Off representation [31]

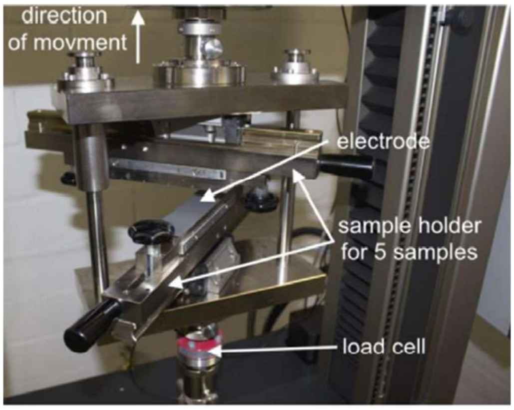


Figure 3.11 Photo of the pull-off setup in a UTM. [31]

There are many different possible parameter setups that can be followed. The setup used by Haselrieder et al. [31], is explained in more detail in fig.3.12. In the first phase of the measurement, the specimen is approached, (t < 2s). Then the compression phase is initiated after contact (2s ≤ t < 9s). In this phase, the compression stress rises until a defined value. Once this value is reached, the stress value is kept constant during a defined dwell time (9s ≤ t < 28.88s), so that the adhesive contact with the electrode is achieved. The final phase is the pull-off phase (38.88s ≤ t < 39s) in which the maximum tensile force is recorded. [31] The adhesion strength σ_n is calculated as:

$$\sigma_{n}=\frac{|F_{t,max}|}{A} \qquad \textit{Eq.3.5}$$

where, $F_{t,\,max}$ is the maximum tensile force, and A is the sample size (equal to the loaded area). [31]

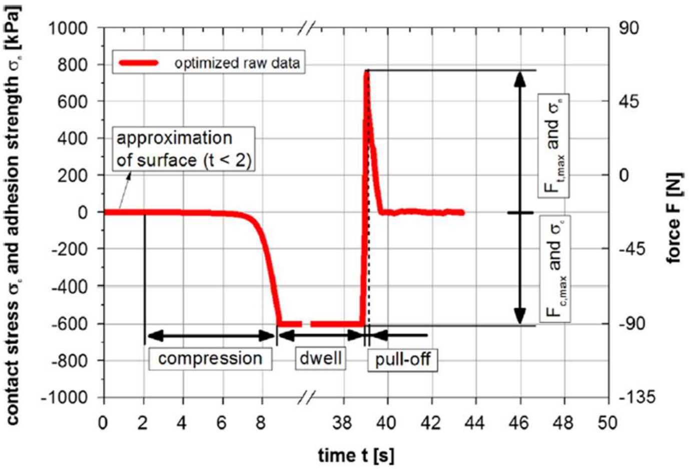


Figure 3.12 Adhesion strength measurement procedure in a pull-off test [31]

The parameters that affect adhesion strength measurement in the pull off test are data acquisition rate, contact (compression) stress, dwell time and pull-off velocity. The higher the compression strength, the higher the adhesion strength. Dwell time is also a very important factor. Without it, insufficient contact between adhesive and the electrode would be achieved, resulting in a lower adhesion strength measured. The adhesion strength is maximized for a contact of at least 30s, according to Haselrieder et al. [31]

This test is suitable when the adhesion between coating and substrate is not too high, the limiting factor is the adhesion between the coating and the tape. An important point to verify is that the loading is purely normal and that no bending takes place at the interface. [37]

A big advantage of this test, with respect to the peel test is that it is possible to measure consecutively, in a rapid manner, 5 specimens per each specimen preparation (electrode strip). This drastically decreases the overall time to perform this test.

3.2.5 Surface and Interfacial Cutting Analysis System (SAICAS)

Another attempt to avoid using the peel test is represented by the (SAICAS). In fact, it has been highlighted that the peel test might depend on the type of adhesive tape used, initial adhesion status between tape and sample surface, the mechanical sensitivity of the UTM, etc. Moreover, the adhesion strength indicated by the peel test is mainly derived from the surface adhesion property rather than the bulk material or the interface between electrode coating and current collector.

The SAICAS system is able to measure the adhesion strength or energy of a coating layer upon various substrates, being an effective and promising tool to measure the coating adhesion of LIB electrodes. In this system a boron nitride blade with a width of 1 mm is used, having a shear angle of 45°. During the test the blade moves horizontally at 0.05 μm/s. In the first step of the process, called cutting mode, the blade moves also vertically with a force of 0.5 N until it reaches the Cu foil. In the second step, called peel mode, the vertical force is reduced to 0.2 N. The adhesion strength is then calculated averaging the horizontal forces during the peel mode, divided by the blade width. [47]

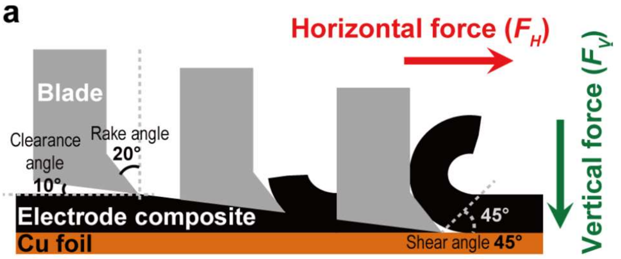


Figure 3.13 Representation of the SAICAS system [47]

3.3 Aim of the project

The aim of this thesis project is to find the best testing setup to measure the adhesion of the interface coating/metallic foil of electrodes for LIBs as a quality control inspection in a production-oriented laboratory. In fact, there is no specific standard (ISO/ASTM) for this kind of adhesion test yet. Coating adhesion strength of LIBs electrodes is a very important mechanical property as it affects the electrochemical lifetime, cycle performance and stability of battery cells.

The 90° peel test is going to be investigated, along with the z-direction pull test and a comparison of the two with the 180° peel test (which was validated prior to this project) is going to be done.

The other two tests mentioned, the T-peel test and the SAICAS system, are not investigated in this project due to lack of time and absence of the right tools to perform them.

4. Method development

This chapter describes the method development efforts performed to define the most suitable specimen preparation procedure and test method for the 90° peel test and the z-direction pull test, both investigated in this thesis project as electrode adhesion strength measurement methods. The procedure used to prepare the specimens should be such as to minimize variations in the results.

4.1 Materials used

All the experiments that are going to be described in this section were performed on pressed anode sheets obtained from production rolls. The central part of the sheet was always investigated (the coating adhesion is not homogeneous along all the width of the sheet) mainly on the so called "side A" of the sheet. In fact, as described in the previous chapter, the copper foil is coated on both sides; at Northvolt, the process is done in two steps. The first side is coated, then dried by passing in the oven. Once dried, the other side of the foil is coated and then dried by passing in the oven. In this way there is a side of the coating that passes in the oven twice, this side is what we call A side and has the lower adhesion. It is possible to recognize the two sides observing the copper foil on the edge: on B side the foil is much shinier than on the other side.

Recap of materials of the anode: the foil is copper, the active material is graphite, CMC is the binder (sometimes used also SBR) and the solvent is deionized water.

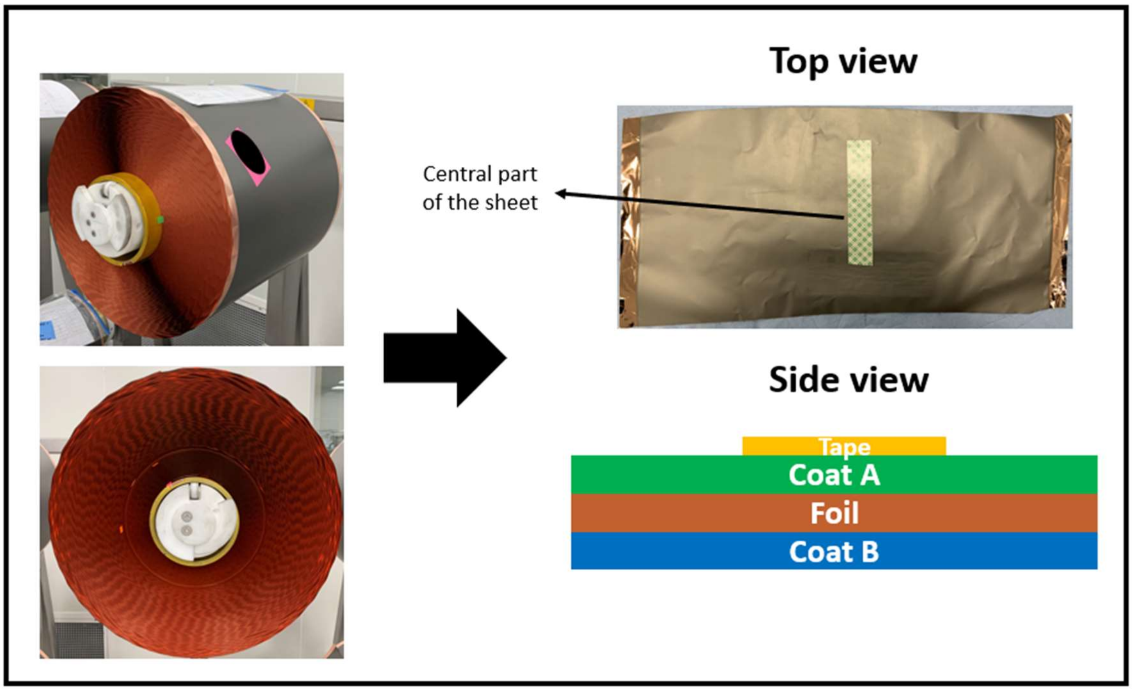


Figure 4.1 Photos of a production electrode roll (left) and of the double-sided tape on the central part of a pressed anode sheet and a representation of the side view of a sheet with the tape on it (right).

The tapes that have been used in the experiments were double-sided adhesive tapes, both in the size of 1 inch wide (25.4mm). To better understand the characteristics of each tape the figure 4.2 is presented.

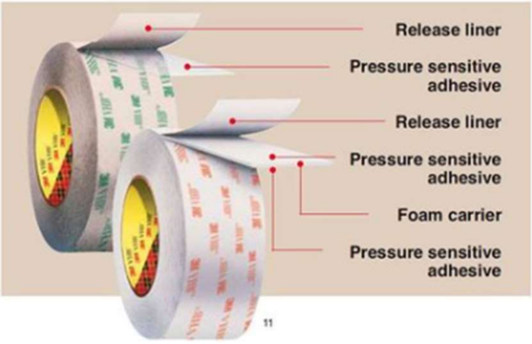


Fig.4.2. Double coated tape construction [55]

The tape used were:

- 3M 410M: the characteristics of this tape are shown in the table 4.1

Table 4.1 Characteristics of the 3M 410M tape [56]

Adhesive Type	**Natural Rubber**
Adhesive Family	860 (3M™ Adhesive 860 is a soft rubber-resin pressure-sensitive adhesive system and features high initial adhesion and good holding power to a wide variety of materials.)
Adhesive Carrier (Backing material)	Treated Paper
Liner	Paper
Liner Thickness	0.075 mm
Total Tape Thickness	0.15 mm
90° Peel Adhesion Stainless Steel	5.6 N/cm

- Tesa 4970:

Table 4.2 Characteristics of the Tesa 4970 tape [57]

Elongation at break	20 %
Type of liner	glassine
Weight of liner	82 g/m^2
Backing material	**PVC film**
Type of adhesive	**tackified acrylic**
Colour of liner	brown
Tensile strength	38 N/cm
Total thickness	225 µm
Thickness of liner	71 µm
Colour	white

4.2 The 90° peel test method

4.2.1 Lessons learned from the 180° peel test method

The 180° peel test method had already been developed and validated prior to this project. Efforts had been made to find the best specimen preparation procedure to ensure the least variation during testing. It was found that the coating on one side of the electrode must be removed in order to obtain reproducible and reliable measurement data.

The steps for the specimen preparation in the 180 degrees peel test are:

1) a piece (13.5cm roughly) of double-sided adhesive tape is placed on the electrode
2) the taped part is pressed three times with a roller
3) the specimen is cut using a cutting die and cutting press
4) the coating on the opposite side of where the tape is stuck is removed using soap
5) the specimen is stuck to a metallic plate through to the double-sided tape
6) the specimen stuck to the plate is pressed once again three times with a roller
7) the plate with the specimen is inserted in the lower grip of the peel test fixture
8) the foil is partially detached from the lower coating and clamped to the grips of the tensile tester
9) the test is finally started

Almost the same identical steps have been adopted for the 90 degrees method, as will be seen in the next section. The need to remove the coating was however investigated again, since it would be great to gain time as the test takes quite a long time to be performed.

The test speed used in the 180° peel test is 50 mm/min. Other speeds such as 25 and 75 mm/min were also investigated and the conclusion was that changing the speed does not make much of a difference. The same speed of 50 mm/min is used as well for the 90° peel test method, as will be seen in the next section.

Only the 3M tape had been investigated during the 180° peel test method development. For the 90° peel test, first measurements were performed with the 3M tape, but to investigate if the tape affects somehow the measurements, new tests with the Tesa® tape were also performed. A separate section is dedicated to this investigation.

The 180° peel test setup is easier to prepare and takes less time compared to the 90° peel test. Mainly this is due to the fact that the weight of the lower fixture is much less and there is no need to use a wire, that adds a variable to the test.

The reason why we want to investigate the 90° peel test setup is because, according to literature, since the bending angle is less the contribution of the plastic yielding to the recorded adhesion force value should be lower. This suggests the possibility to obtain the true adhesion strength in a reliable and reproducible way, without having to remove the coating and, in any case, a "cleaner" measurement with or without the coating.

Table 4.3 Advantages and disadvantages of the 180° peel test.

180° peel test	
Advantages	Disadvantages
-Setup easy and quick to prepare -Low weight of the lower grip -Foil easy to clamp in the upper grip -No wire needed	-Long time to prepare the specimen (due to one-sided coating removal) -Since the bending is very high, the measurement might be affected by the plastic yielding

4.2.2 Effect of coated versus non-coated specimen in the 90° peel test setup

To find the best method to prepare specimens for the 90° peel test method, twenty-four measurements were performed on the central part of pressed anode sheets all originating from the same production electrode roll. Both A and B side was investigated as well as coated and non-coated specimens. This results in the following types of specimens:

Table 4.4 Types of specimens measured

Side of the anode sheet	A	B
Number of coated specimens	6	6
Number of uncoated specimens	6	6

Since the method for the 180° peel test had already been developed prior to this project and the 90° peel test is very similar, the specimen preparation of the 180° peel test described in the section above was kept identical also for this test setup. The main goal of this investigation was to find out if one side of the coating must also be removed (as it is done for the 180° peel test) when performing this test or if there is no need to remove the coating, allowing to save time during specimen preparation and, hence, possibly make this test setup more attractive as a quality control inspection in a production-oriented laboratory.

Specimen preparation steps:

1) a piece of double-sided adhesive tape is placed on the electrode
2) the taped part is pressed three times with a roller
3) the specimen is cut using a cutting die and cutting press
4) the coating on the opposite side of where the tape is stuck is removed using soap (only for "uncoated specimens", for the "coated specimens" this step is skipped)
5) the specimen is stuck to a metallic plate thanks to the double-sided tape
6) the specimen stuck to the plate is pressed once again three times with a roller
7) the plate with the specimen is inserted in the carriage of the peel testing fixture
8) the foil is partially detached from the lower coating and clamped to the grips of the tensile tester
9) the test is finally started

For each measurement the force value needed to separate the foil from the coating is recorded in the UTM software report for four different travel regions: 10-20 mm, 20-30 mm, 30-40 mm, 40-50 mm. This force is the average value of many values recorded in each travel region. For each travel region (range) the standard deviation is also recorded, allowing to determine how accurate the measurement is in that travel region. It can also be defined as the "natural variation of the process". A low standard deviation value of the range (<0.003) means high accuracy (reliability) of the force value, resulting in a more linear curve on the graph. When the standard deviation of the range is very high, peaks on the curve graph are observed.

In the peel test graph reports, curves in the lower part of the graph (near to the x axis) can be noticed: they represent the "second run" of the test, done on the same specimen to record the weight of the foil. The final adhesion force is calculated as the force recorded on the first measurements (curves on the upper part of the graph) minus the weight of the foil.

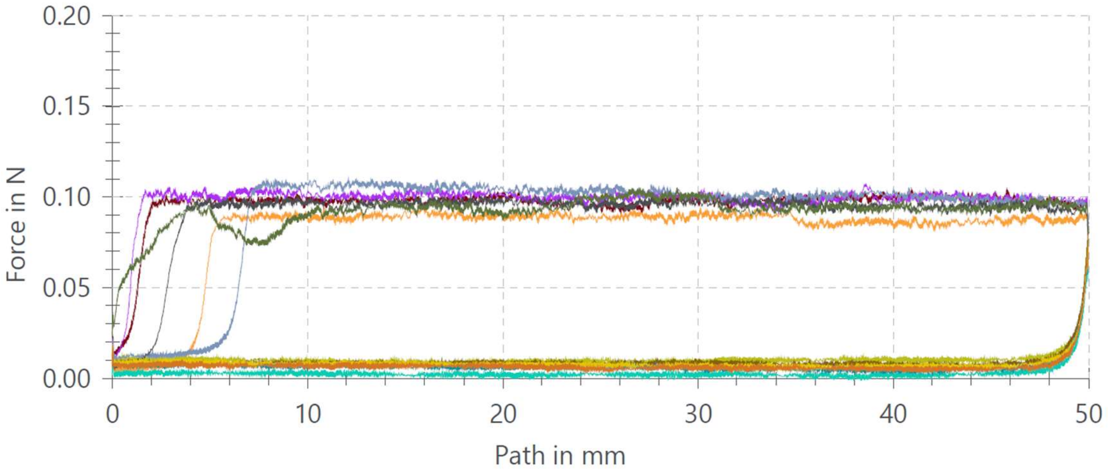


Figure 4.3 Graph of the A side without coating

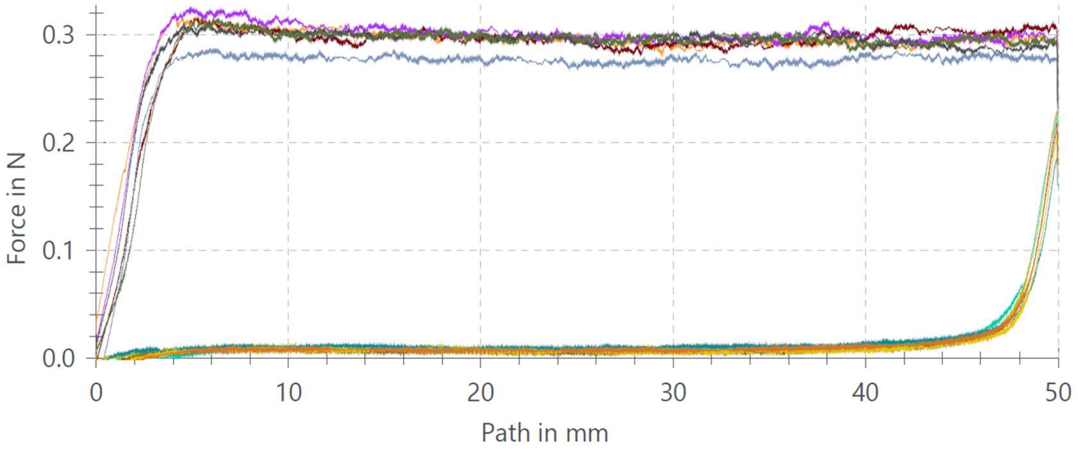


Figure 4.5 Graph of the A side with coating

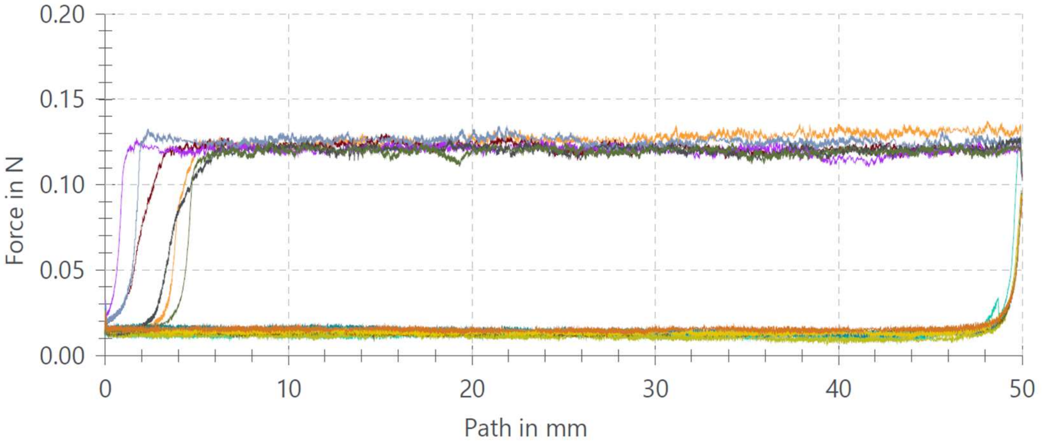


Figure 4.6 Graph of the B side without coating

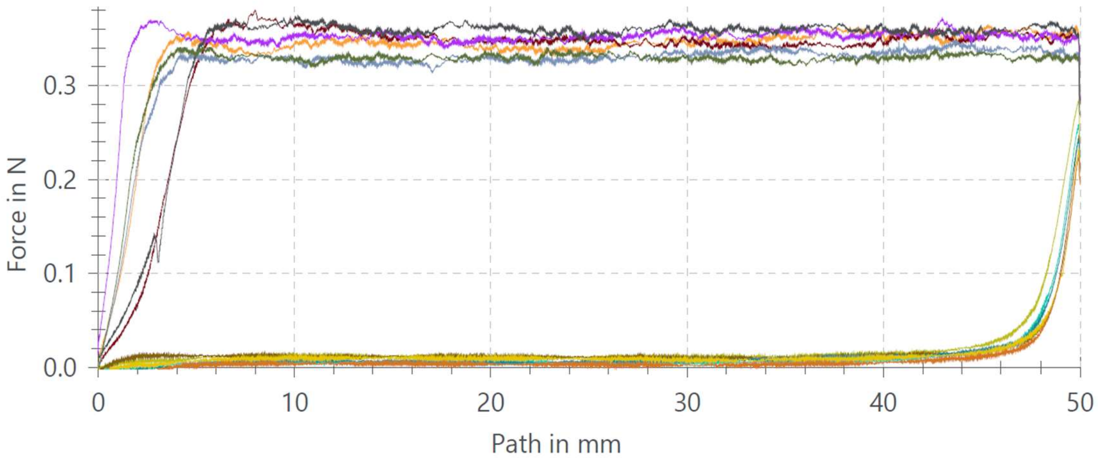


Figure 4.7 Graph of the B side with coating

According to the data (it is not always clear just from the graphs), for these measurements the most accurate travel region was found to be the 20-30 mm travel region range. Therefore, all the values reported in the following table are referring to this travel region.

Table 4.5 Adhesion force and Sdev values of A-B sides both coated and uncoated

	A side uncoated	A side coated	B side uncoated	B side coated
Force value 1 [N]	0.087	0.288	0.114	0.336
Force value 2 [N]	0.088	0.285	0.111	0.336
Force Value 3 [N]	0.092	0.293	0.109	0.341
Force value 4 [N]	0.097	0.269	0.112	0.323
Force value 5 [N]	0.090	0.291	0.108	0.35
Force value 6 [N]	0.092	0.289	0.106	0.328
Sdev avg of the range	0.0023	0.0035	0.0023	0.0035
Force avg [N]	0.091	0.286	0.110	0.336
Sdev of the force values	0.0036	0.0087	0.0029	0.0095
Sdev%	3.96	3.04	2.64	2.83

Some conclusions that can be drawn from the data in table 4.5:

1) A side is weaker than B for both coated and uncoated specimens. This is due to the production process. It is well known but it is good to observe for two reasons: the recorded values should be reliable and it is useful to highlight it for the following paragraph about the z-direction pull test.
2) The standard deviation of the range is higher for coated specimens for both A and B sides, and the average value is higher than 0.003. This means that the force value recorded is less accurate (and therefore less reliable).
3) The standard deviation of the force is always lower in the uncoated specimens for both side A and B. But, if we consider the standard deviation in percentage, no clear trend is observed. Removing the coating is recommended, but should be further investigated. A measurement system analysis on both cases could clear this.
4) The force values recorded for the coated specimens is much higher (three times higher, more or less) than the uncoated specimens. Literature suggests that the coating could be

kept because the bending is less than in the 180° peel test, and therefore the contribution of plastic deformation to the recorded force value could be negligible. But, since the difference is so high, the value recorded in the coated specimens should not be the true value of the adhesion force between coating and foil.

4.2.3 Effect of the double-sided adhesive tape type

The aim of this section is to investigate if the tape affects the recorded adhesion force.

The coating adhesion of pressed anode sheets was measured using the Tesa tape only on A side for both coated and un-coated specimens. Twelve specimens were tested for each specimen preparation. The sheets investigated were all from the same roll (batch).

In the following table (4.6) the average force and standard deviations of both coated and uncoated specimens tested on side A with both tapes are reported. The sheets investigated for the 3M were the same for coated and uncoated specimens but were different from the ones investigated with the Tesa tape.

Table 4.6 Values of adhesion and standard deviation for coated and uncoated specimens tested on side A with both adhesive tapes

	Tesa tape		3M tape	
	A side uncoated	A side coated	A side uncoated	A side coated
Force value 1 [N]	0.086	0.393	0.087	0.288
Force value 2 [N]	0.082	0.368	0.088	0.285
Force value 3 [N]	0.082	0.415	0.092	0.293
Force value 4 [N]	0.088	0.398	0.097	0.269
Force value 5 [N]	0.094	0.387	0.090	0.291
Force value 6 [N]	0.083	0.412	0.092	0.289
Force value 7 [N]	0.079	0.442	-	-
Force value 8 [N]	0.089	0.39	-	-
Force value 9 [N]	0.088	0.418	-	-
Force value 10 [N]	0.086	0.403	-	-
Force value 11 [N]	0.087	0.383	-	-
Force value 12 [N]	0.083	0.393	-	-
Sdev avg of the range	0.0022	0.0041	0.0023	0.0035
Force avg [N]	0.086	0.4	0.091	0.286
Sdev of the force values	0.004	0.0194	0.0036	0.0087
Sdev%	4.65	4.85	3.96	3.04

Conclusions on the effect of the adhesive tape on the recorded values:

- The average force and standard deviation for the uncoated specimen is similar
- The average force and standard deviation for the coated specimens is quite different
- For the uncoated specimens no influence of the tape is observed
- Further investigation should be done to understand why there seems to be no effect on uncoated specimens, while there seems to be on coated ones.
- The standard deviation is lower in values for uncoated specimens, while in percentage is similar for the Tesa specimens, different for the 3M (and lower for the coated).

- The average standard deviation of the range is lower for the uncoated specimens.

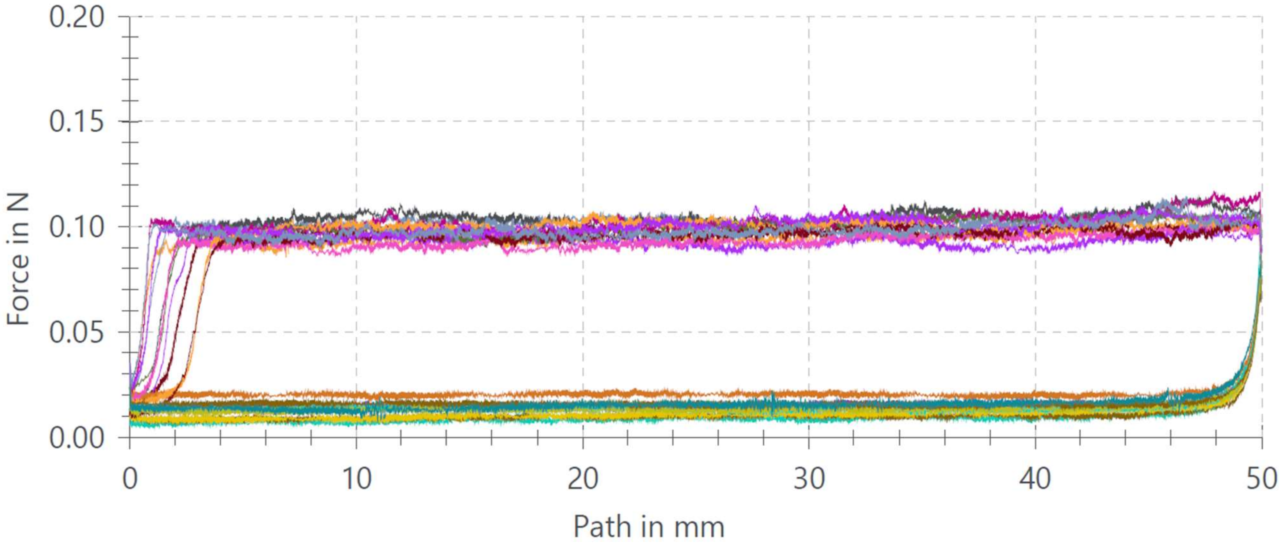


Figure 4.8 Graph of the uncoated specimens tested with the Tesa tape

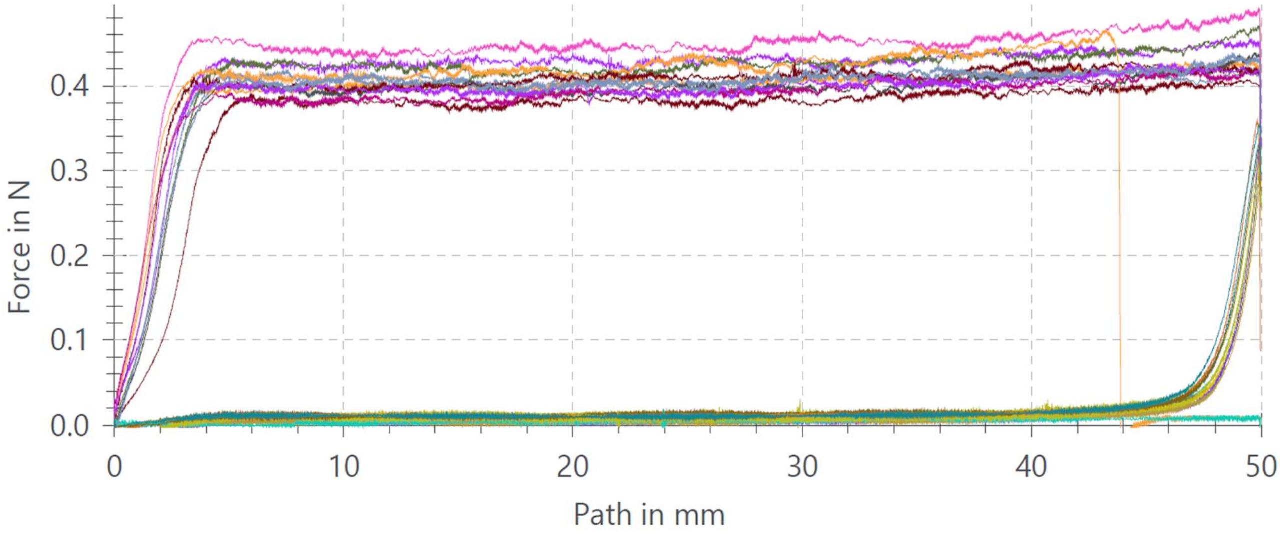


Figure 4.9 Graph of the uncoated specimens tested with the Tesa tape

4.3 The z-direction pull test method

This section focuses on the method development efforts performed on the z-direction pull test method as a potential test setup to be carried out in a production environment to assess the adhesion strength of battery electrodes. Measurements were performed to first get familiar with the measurement setup as well as to understand more about the effect of specimen preparation and test setup parameters on the adhesion of the electrode specimens.

4.3.1 Introduction to the z-direction pull test on electrodes

The aim of this paragraph is to give a general introduction to the z-direction pull test on electrodes to better understand the efforts undertaken and assumptions and conclusions drawn later in the method development stage of this work.

In general, a piece of double-sided tape (1 inch wide (2,54 cm), 15 cm long) is placed on the electrode, then cut and pressed using a roller. The electrode is then stuck to the bottom grip, while another piece of double-sided tape is stuck to the upper grip. Fig. 4.10 visualises the test setup.

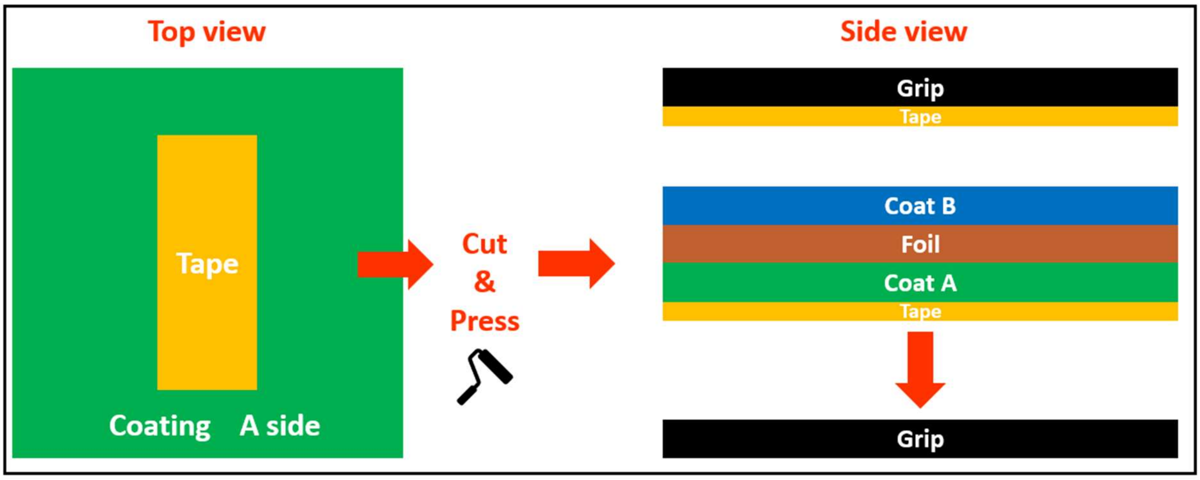


Figure 4.10 Preparation (top view) and test setup (side view)

The side view visualises the two interfaces of the electrode that we are interested in to find out the adhesion strength:

- The A side coating of the electrode with the foil (green-brown interface)
- The B side of the electrode with the foil (blue-brown interface)

The grips are then placed in the z-direction pull test fixture of the tensile tester after which the test is started. The test itself comprises of first a compression step, held for a certain compression time (one of the parameters that will be investigated), followed by a pull off / tensile step. Fig. 4.11 visualises both test steps.

Figure 4.11 Representation of the steps of compression and pull off

Following this test, two different situations can then either be observed. In the first one (fig. 4.12 left) the detachment is observed between coating A and the foil, while in the second situation (fig. 4.12 right) the detachment is observed between coating B and the foil.

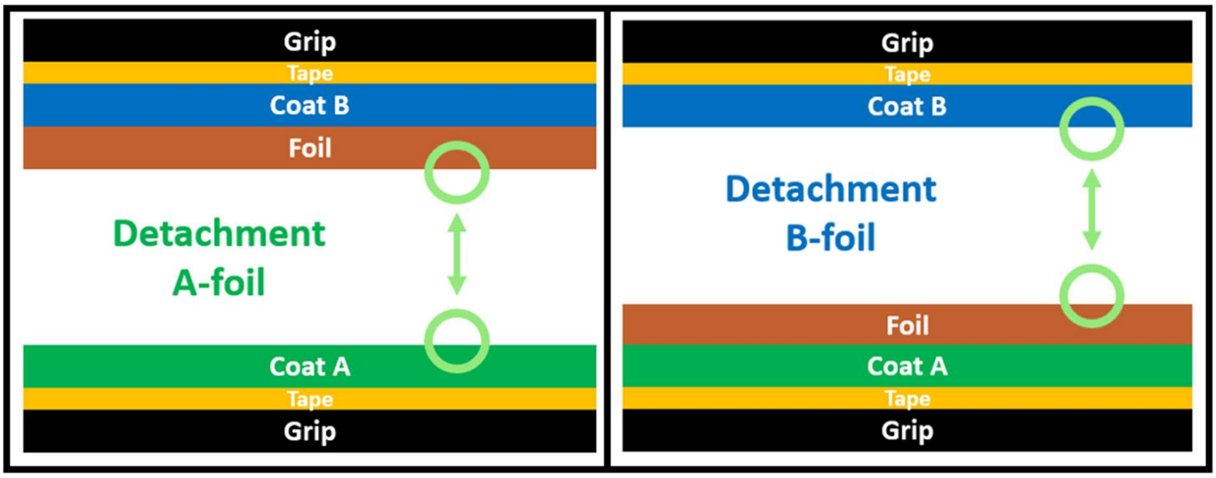


Figure 4.12 Representation of a detachment between the foil and the A side of the coating (left) and between the B side of the coating and the foil (right)

At first it was thought that a “test failure” is when the detachment is observed on the opposite interface of the pressed side. For example, when pressing with the roller A side and placing the A side on the lower grip, but getting the detachment at the interface of coating B and the foil. However, as will be shown further on, the detachment in near to all our tests mostly occurs between coating A and foil, regardless of which side is the pressed side. Mainly this is because, no matter which side is pressed, the detachment should always occur at the weakest interface of the specimen. We know from the peel test measurement results that A is always the weaker side, which is also the expected weaker side due to the way that the electrode rolls are produced. Hence, the results obtained in the z-direction pull test method are in in accord with the measurements done in both types of peel tests.

Hence, will refer from now on to a “failure” in this test setup if the detachment of the coating B – foil interface (strongest interface) occurs during testing.

An example of the graph that the software shows when performing the test is presented in fig. 4.13. The test time in seconds is on the x axis and helps to visualise the different steps on the process, while the tensile force in Newton is on the y axis.

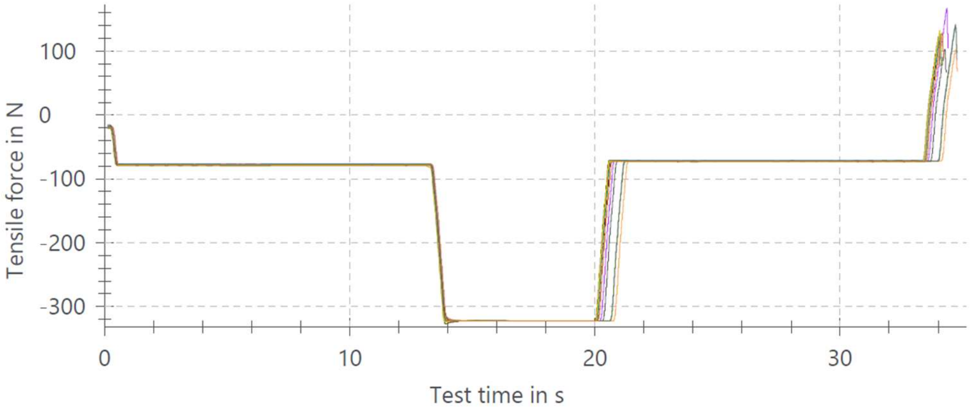


Figure 4.13 Example of graph of a z-direction pull Test

4.3.2 Effect of specimen preparation

Different specimen preparations have been tried. In this section a brief overview of the top 5 sample preparation methods is given to better understand the measurements that are explained further on in this chapter.

1. Method 1 (“Cutting die + big roller”): the tape is placed on the electrode and rolled with the “Big roller”, then cut to obtain the strip using a cutting press and die, the strip is stuck to a grip and finally the different squares are cut using a cutter.
2. Method 2 (“Cutting die + little roller”): the tape is placed on the electrode, then cut using a cutting press and die, stuck to the grip, rolled with the “little roller” and the final squares are cut using a cutter.
3. Method 3 (“Cutter + big roller”): the tape is placed on the electrode and rolled with the “Big roller”, then cut to obtain the strip using a cutter, the strip is stuck to a grip and finally the different squares are cut using the same cutter.
4. Method 4 (“Cutter + little roller”): the tape is placed on the electrode, then cut using a cutter, stuck to the grip, rolled with the “little roller” and the final squares are cut using the same cutter.
5. Method 5 (“Electrode on tape + cutter + little roller”): the tape is stuck to the grips first, then the electrode is stuck to one of them, the edges are cut using a cutter and rolled using the “little roller” and the squares are obtained using the same cutter.

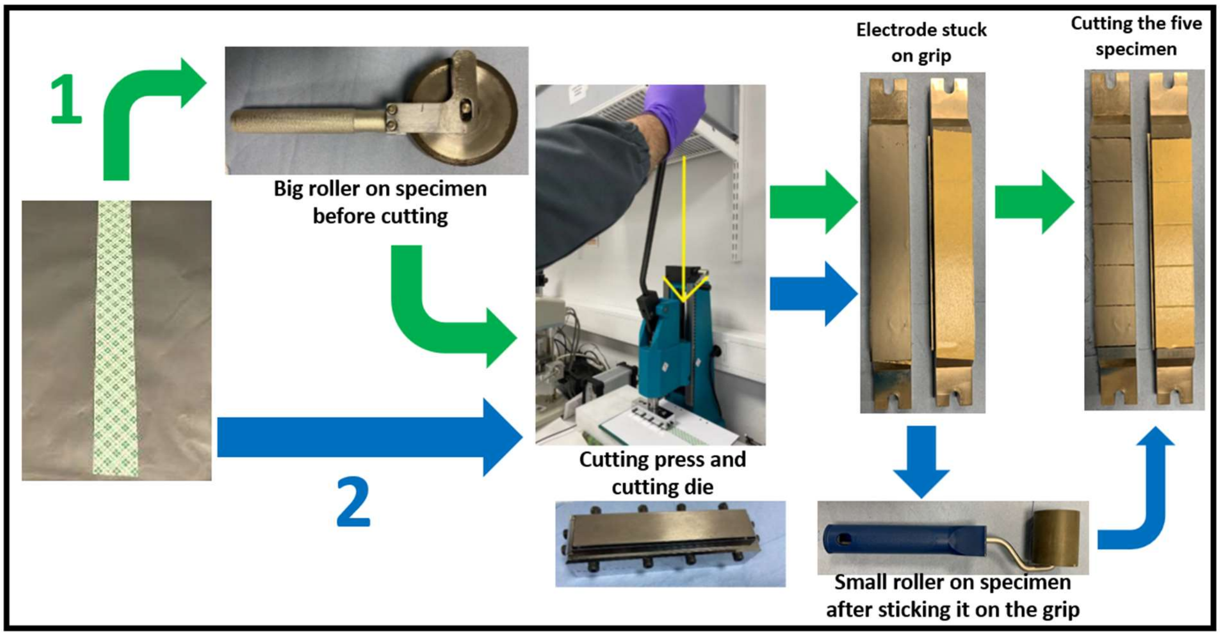


Figure 4.14 Steps for method 1 (arrows in green) and method 2 (arrows in blue)

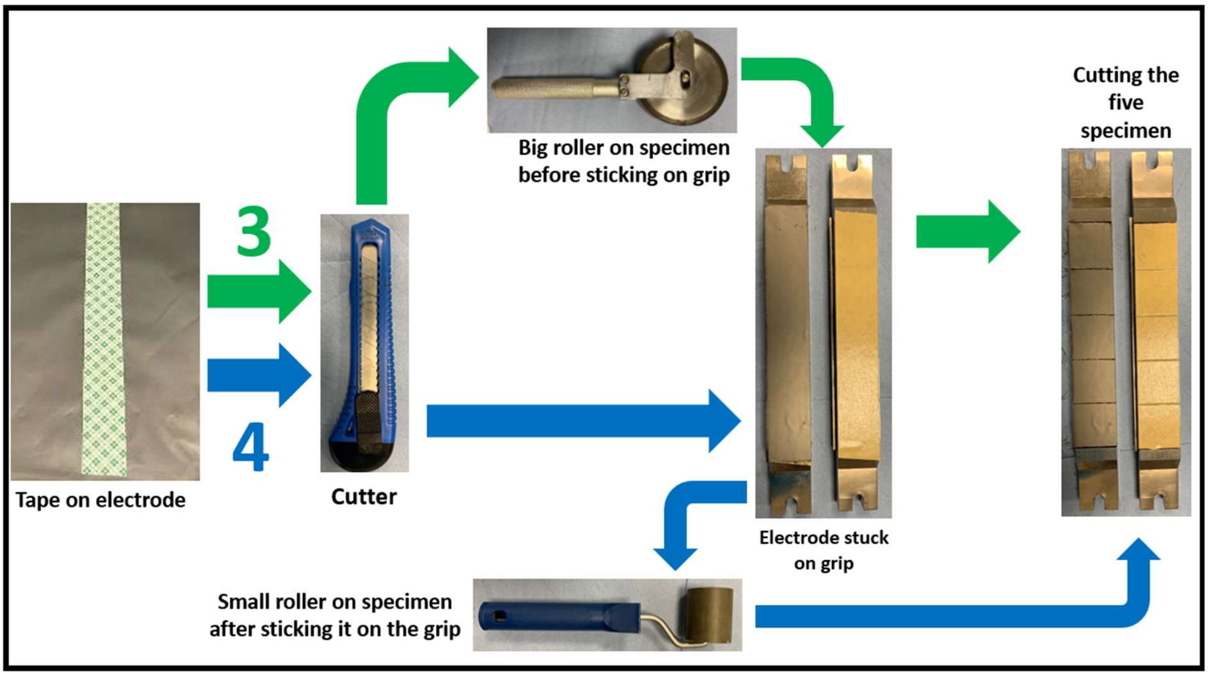


Figure 4.15 Steps for method 3 (arrows in green) and method 4 (arrows in blue)

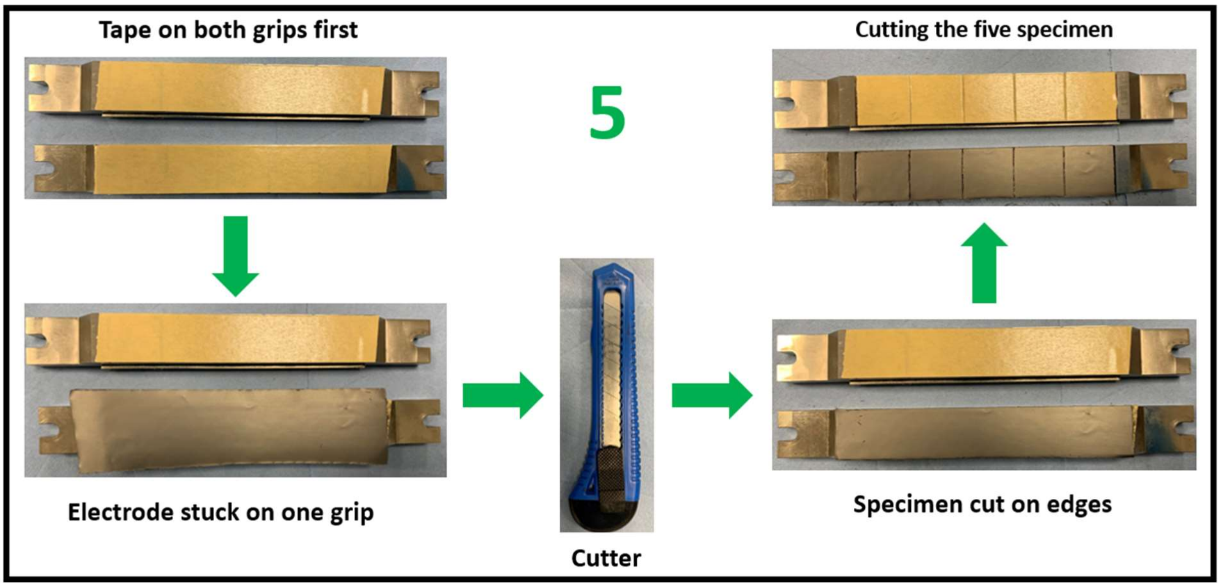


Figure 4.16 Steps for the "Electrode on tape + cutter + little roller"

To investigate the best specimen preparation method, three sets of measurement were performed. In all cases the tape was placed on the centre part of the A side of the electrode sheet and pressed on the same side. For each set of experiments, sheets from the same roll (same batch) were used. All measurements were performed keeping following constant parameters:

- Compressive loading: 0.5 MPa
- Hold time under compressive loading: 6 s
- Test speed: 10 mm/min

First set of experiments

Table 4.7 Results from the first set of experiments, the values that were failures are shown in brackets

	Method 1	Method 2	Method 3	Method 4	Method 5
Max. tensile Force 1 [N]	154.4	173.8	130.7	144.1	189.3
Max. tensile Force 2 [N]	169.3	152.5	148.8	156.5	(45.9)
Max. tensile Force 3 [N]	171.1	154.1	154.0	138.6	(206.1)
Max. tensile Force 4 [N]	169.5	164.0	151.5	163.2	138.8
Max. tensile Force 5 [N]	-	-	161.2	-	-
Avg max. tensile force [N]	166.1	161.1	149.2	150.6	186.6
Sdev	7.8	9.9	11.3	11.3	3.9
Sdev%	4.7	6.1	7.6	7.4	2.1
Number of failures	0/4	0/4	0/5	0/4	2/4 (50%)

Method 5 was discarded after this first set of experiments. The standard deviation is very low but calculated on only two values. The choice to not further investigate the method was based mainly on the fact that it is difficult to obtain a good alignment of the electrode on the grip (the adhesion should be tested along a straight line of the electrode).

Second set of experiments

Table 4.8 Results from the second set of experiments (failures shown in brackets)

	Method 1	Method 2	Method 3	Method 4
Max. tensile Force 1 [N]	188.5	167.4	182.3	(171.8)
Max. tensile Force 2 [N]	184.7	180.4	100.9	(159.7)
Max. tensile Force 3 [N]	(176.1)	152.8	167.3	155.1
Max. tensile Force 4 [N]	(174.3)	151.7	(163.8)	138.5
Max. tensile Force 5 [N]	172.5	179.5	162.3	162.7
Max. tensile Force 6 [N]	165.1	174.9	161.6	157.4
Max. tensile Force 7 [N]	171.8	163.5	(177.7)	167.3
Max. tensile Force 8 [N]	(156.4)	154.1	160.2	168.0
Max. tensile Force 9 [N]	159.4	182.2	153.2)	169.7
Max. tensile Force 10 [N]	166.7	179.0	136.9	154.3
Max. tensile Force 11[N]	179.5	181.0	192.3	191.7
Max. tensile Force 12 [N]	178.5	157.9	176.6	154.6
Max. tensile Force 13 [N]			154.2	190.9
Max. tensile Force 14 [N]			153.3	168.0
Avg max. tensile Force [N]	174.1	168.7	158.9	164.9
Sdev	9.5	12.2	24.4	15.1
Sdev%	5.5	7.2	15.4	9.2
Number of failures	3/12 (25%)	0/12 (0%)	3/14 (21.43%)	3/14 (14.3%)

Conclusions from the second set of experiments:

- Using the cutting die (method 1 and 2) allows to get a lower Sdev compared to using the normal cutter (method 3 and 4).
- A lower Sdev is obtained using method 1 (9.54) compared to method 2 (12.18), but no failures occurred (0/12) with this method, while 3 failures out of 12 measurements

occurred using method 1. It has to be considered that it is easier to have a higher Sdev with 12 values than 9.

Figure 4.17 Specimens tested with method 1, the three failures are circled in red

Figure 4.18 Specimens tested with method 2, no failures occurred as can be observed

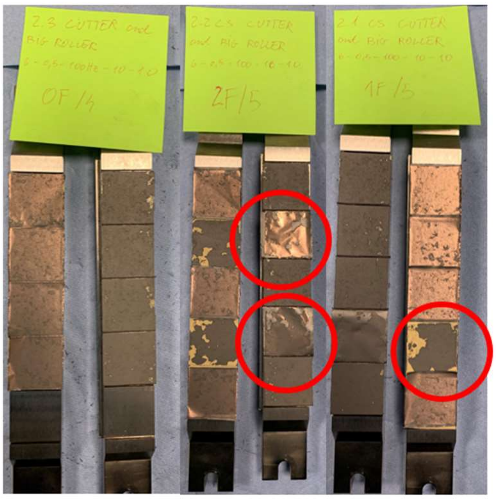


Figure 4.19 Specimens with method 3 (3 failures highlighted)

Figure 4.20 Specimens tested with method 4

Third set of experiments

A third set of experiments was performed on a different batch, the same methods as set 2 were performed. The aim was to take a final decision on which method is best between 1 and 2, since based on the previous experiments method 1 has the lowest standard deviation, but number 2 has the lowest number of failures. Method 3 and 4 are tested just for a double check.

Table 4.9 Results from the third set of experiments

	Method 1	Method 2	Method 3	Method 4
Max. tensile Force 1 [N]	101.9	141.8	(114.4)	115.2
Max. tensile Force 2 [N]	124.2	109.4	(115.4)	88.0
Max. tensile Force 3 [N]	(120.8)	127.8	140.1	113.7
Max. tensile Force 4 [N]	(126.7)	127.0	(138.9)	121.5
Max. tensile Force 5 [N]	167.2	136.2	103.5	146.7
Max. tensile Force 6 [N]	(122.9)	134.0	(136.5)	114.0
Max. tensile Force 7 [N]	(142.0)	102.0	118.3	135.8
Max. tensile Force 8 [N]	126.9	123.2	140.5	133.6
Max. tensile Force 9 [N]	103.2	103.4	120.7	119.0
Max. tensile Force 10 [N]	132.9	139.0	132.8	110.6
Max. tensile Force 11[N]	140.4	136.2	138.9	115.4
Max. tensile Force 12 [N]	129.4	125.2	(126.8)	101.5
Max. tensile Force 13 [N]			129.4	94.3
Max. tensile Force 14 [N]			87.9	122.2
Avg max. tensile Force [N]	128.3	125.4	123.6	116.5
Sdev	20.8	13.7	18.1	15.7
Sdev%	16.2	10.9	14.7	13.5

Number of failures	4/12 (33.33%)	0/12 (0%)	5/14 (35.71%)	0/14 (0%)

Conclusions from the third set of experiments:

- The average force is similar in the first three cases, a bit lower for method 4.
- Using the little roller (method 2 and 4), no matter the cutting mean, led to 0 failures out of 26 samples, while using the big roller (method 1 and 3) led to 9 failures out of 26 (34.62%).
- The lowest standard deviation and number of failures is obtained with method 2

Figure 4.21 Specimens tested with method 1, the four failures are circled in red

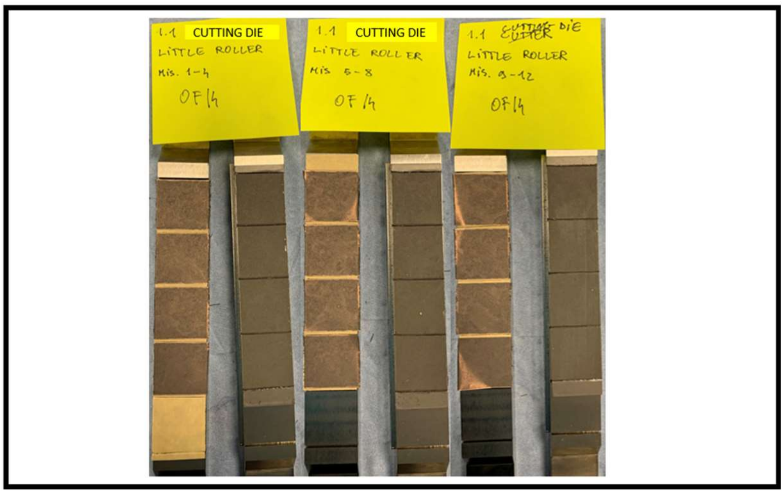


Figure 4.22 Specimens tested with method 2

Figure 4.23 Specimens tested with method 3, the failures are circled in red

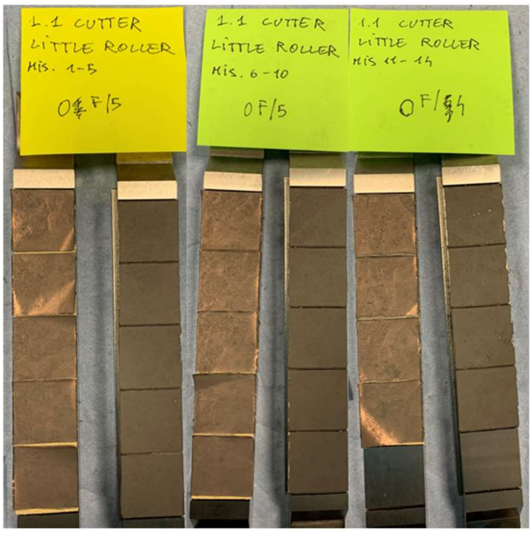


Figure 4.24 Specimens tested with method 4

Conclusions on method preparation

Table.4.10 Overall Sdev and number of failures for each method

	Method 1	Method 2	Method 3	Method 4
Avg Force set 1	166.1	161.1	149.2	150.6
Avg Force set 2	174.1	168.7	158.9	164.9
Avg Force set 3	128.3	125.4	123.6	116.5
Sdev set 1	7.9	9.9	11.3	11.3
Sdev set 2	9.5	12.2	24.4	15.1
Sdev set 3	20.8	13.7	18.1	15.7
Failures set 1	0/4	0/4	0/5	0/4
Failures set 2	3/12	0/12	3/14	2/14
Failures set 3	4/12	0/12	5/14	0/14
Overall Avg Force	156.1	151.7	143.9	144.0
Avg Sdev	12.7	11.9	18.0	14.0
Avg Sdev%	8.2	7.9	12.5	9.8
Total number of failures	7/28	0/28	8/33	2/ 32
% of failures	25	0	24.2	6.3

- Method 1 had the lowest standard deviation in the first two sets of experiments, while very high for the third one.
- The lowest average of the standard deviations is obtained with method 2.
- The lowest number of failures is obtained for method 2.
- Method 2 is the recommended specimen preparation method.

4.3.3 Effect of placing tape on A or B side

To understand which side is best to stick the tape on and press, to have the least number of failures and the most reliable values, two sets of experiments were performed on sheets from the same roll. The same different specimen preparations were tried on both sides, keeping following constant parameters:

- Compressive loading: 0.5 MPa
- Hold time under compressive loading (dwell time): 6 s
- Test speed: 10 mm/min

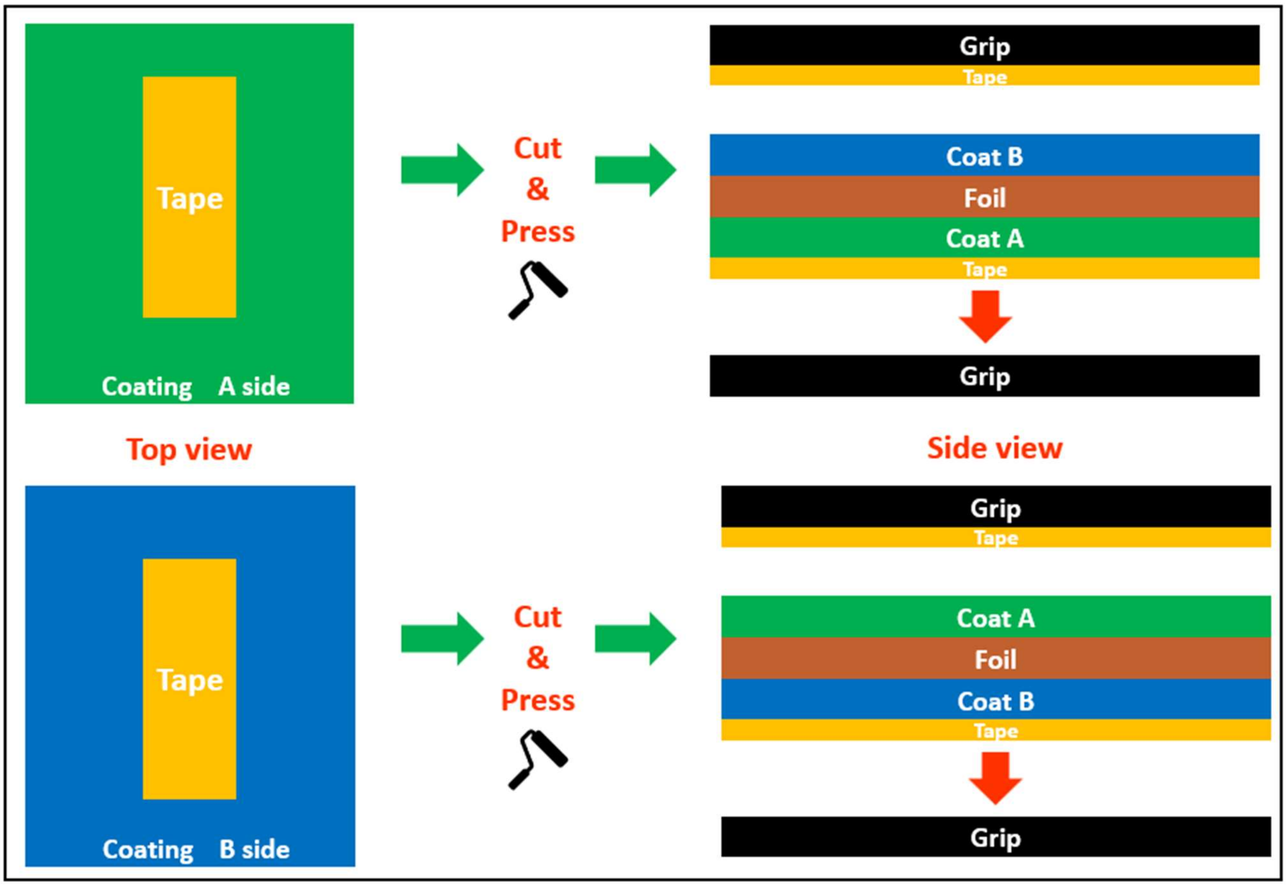


Figure 4.25 Representation of both specimen preparation, the upper one sticking the tape on the A side, the lower one sticking the tape on the B side

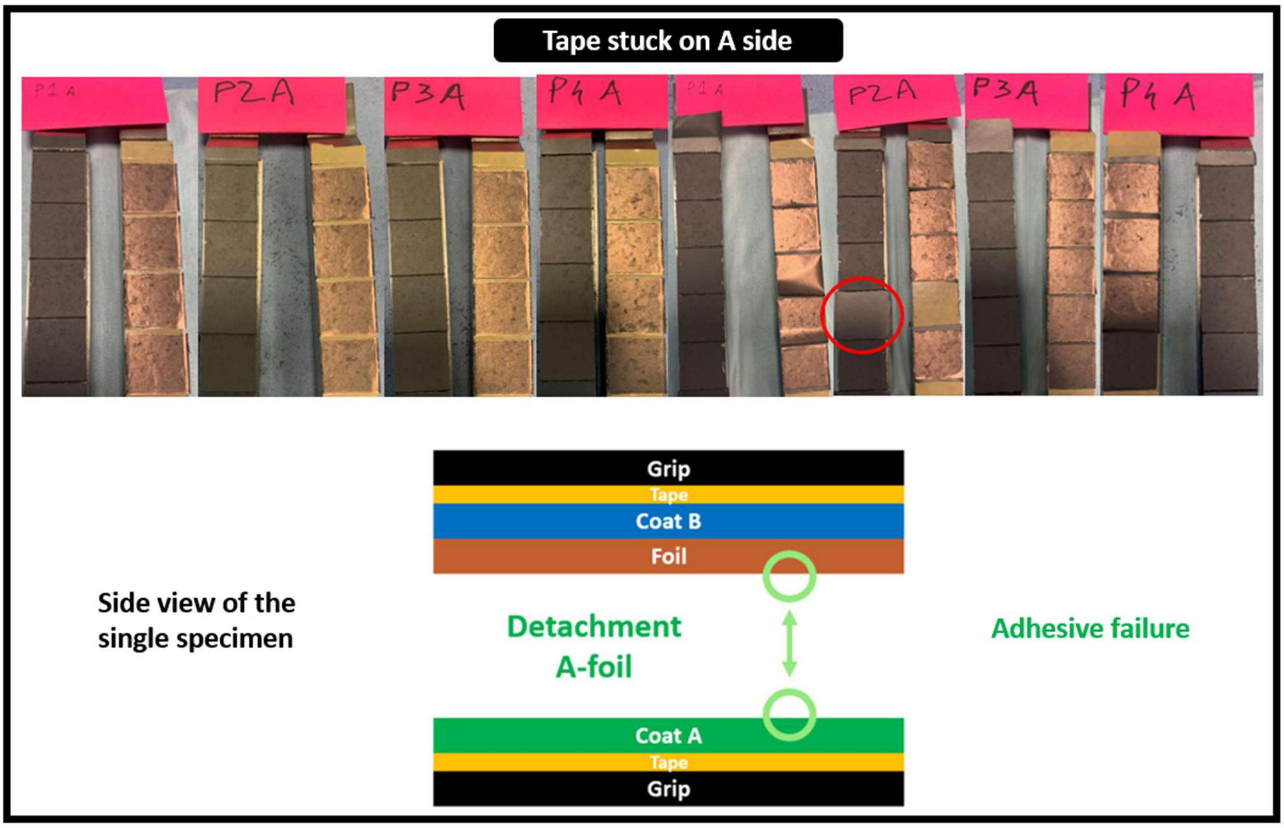


Figure 4.26 Photos of some of the specimen tested when the tape was stuck on the A side of the electrode and the representation of the side view of a specimen after this test

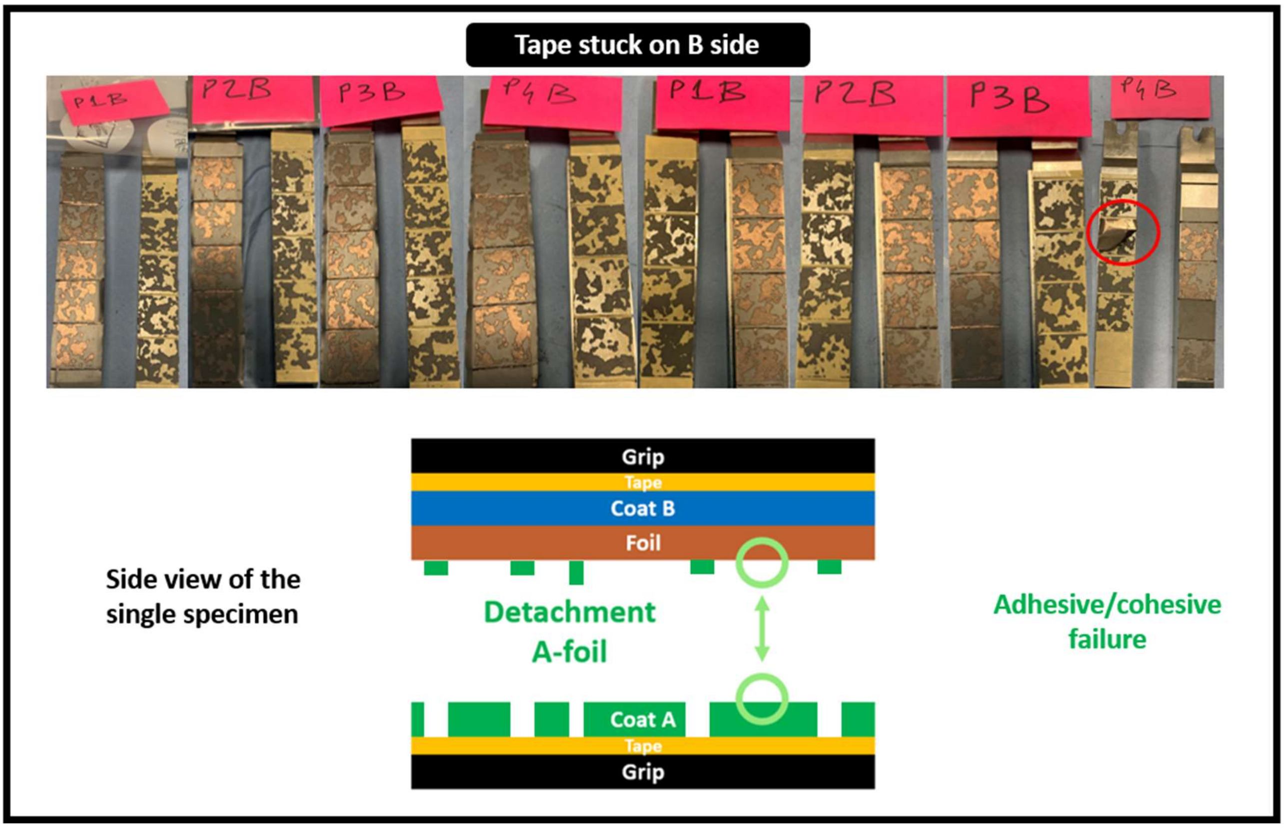


Figure 4.27 Photos of some of the specimen tested when the tape was stuck on the B side of the electrode and the representation of the side view of a specimen after this test

As can be visually observed, only for the specimen prepared sticking the tape on A side a homogeneous detachment foil-coating is obtained at the interface coating A foil. This has been described in literature (and in chapter 3) as an adhesive failure. While, when placing the tape on the B side, a mixture of cohesive and adhesive failure is obtained at the interface coating A foil, not allowing to record the effective value of the adhesion of the interface coating-foil. In fact, the average value of the force recorded is lower when sticking the tape on B side, as shown by table 4.11.

Table 4.11 Results from the 35 measurements on side A and B

	Side A	Side B
Max. tensile force 1 [N]	179.8	127
Max. tensile force 2 [N]	179.6	152.8
Max. tensile force 3[N]	137.9	119.2
Max. tensile force 4 [N]	147.9	129.2
Max. tensile force 5 [N]	159.4	134.4
Max. tensile force 6 [N]	171.2	116
Max. tensile force 7 [N]	134.8	114.8
Max. tensile force 8 [N]	164.1	105.2
Max. tensile force 9 [N]	154.4	130
Max. tensile force 10 [N]	169.3	108.8
Max. tensile force 11 [N]	169.5	121
Max. tensile force 12 [N]	171.1	102.4
Max. tensile force 13 [N]	173.8	128.5
Max. tensile force 14 [N]	152.5	101.9
Max. tensile force 15 [N]	154.1	121.3
Max. tensile force 16 [N]	164	**(118) F**
Max. tensile force 17 [N]	152.8	132.9
Max. tensile force 18 [N]	149.4	123.8
Max. tensile force 19 [N]	**(18) F**	131.4
Max. tensile force 20 [N]	**(96) F**	135.4
Max. tensile force 21 [N]	138.1	102.4
Max. tensile force 22 [N]	165.2	112.6
Max. tensile force 23 [N]	**(1.9) F**	108.1
Max. tensile force 24 [N]	172.9	141.5
Max. tensile force 25 [N]	137.4	115.4
Max. tensile force 26 [N]	158.7	125.3
Max. tensile force 27 [N]	148.8	131.4
Max. tensile force 28 [N]	154	100.3
Max. tensile force 29 [N]	151.5	130.6
Max. tensile force 30 [N]	161.2	125
Max. tensile force 31 [N]	130.7	137.7
Max. tensile force 32 [N]	144.1	107.7
Max. tensile force 33 [N]	156.5	151.5
Max. tensile force 34 [N]	138.6	116.5
Max. tensile force 35 [N]	163.2	129.8
Number of failures	3/35	1/35
Avg max. tensile force [N]	156.5	122.7

Hence, sticking the tape on the A side (the weaker side) of the electrode and pressing with the roller on that side is recommended.

4.3.4 Effect of parameters

To find the best measurement testing parameters to use in the z-direction pull test four different set of experiments were performed using four different parameter setups. The different parameters used in each set of measurements are shown in table 4.12. The tests were performed on different sheets, but the specimen preparation used was always the same, namely method 2. The tape has always been placed on the A side of the coating. The choice to try these parameters came from a mix of suggestions from the operators of the company that sold the tensile tester to Northvolt and knowledge from the literature review.

Table 4.12 Parameters used in each set of measurements

	Setup 1	**Setup 2**	**Setup 3**	**Setup 4**
Compressive stress	0.5 MPa	0.5 MPa	0.6 MPa	0.6 MPa
Dwell time	6 s	6 s	30 s	30 s
Test speed	10 mm/min	100 mm/min	10 mm/min	100 mm/min
Data acquisition rate	2 kHz	2 kHz	2 kHz	2 kHz

Table 4.13 Results of each set of measurement.

	Setup 1	**Setup 2**	**Setup 3**	**Setup 4**
Avg max. tensile force [N]	151.7	-	138.9	-
Avg Sdev	11.9	-	20.3	-
Sdev%	7.8	-	14.6	-
Total failures	0/28	8/8	9/12	8/8
%failures	0	100%	75%	100%

All the results obtained for setup 1 can be found in the previous tables of the method development (section 4.3.2, tables 4.7-9) in the columns "method 2". The results for the other setups are not reported since the number of failures were so high and therefore the visual inspection is more important.

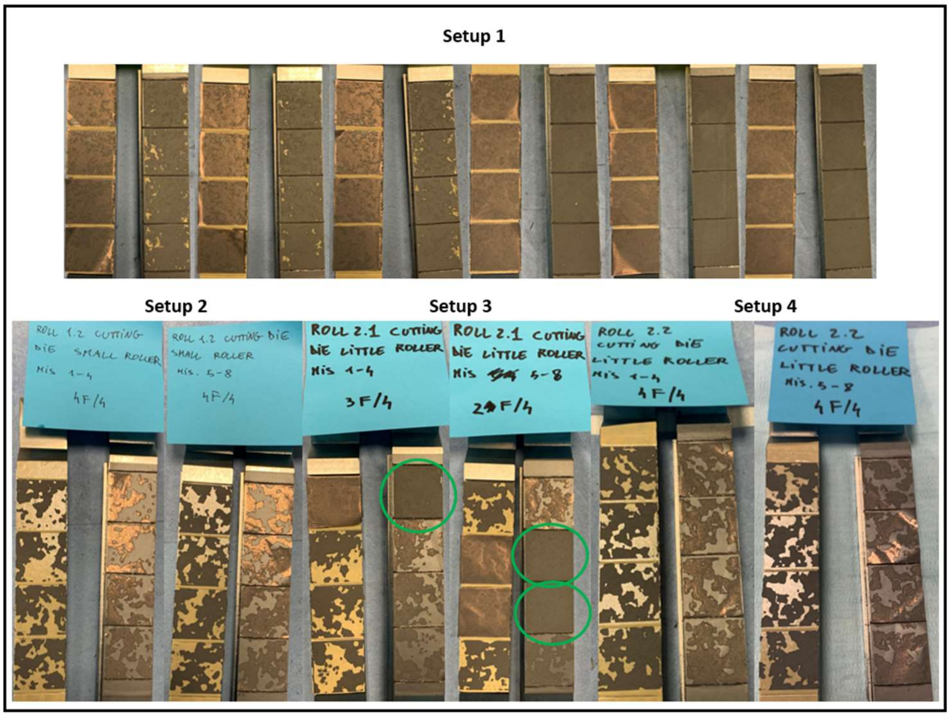


Figure 4.28 Some of the specimens tested with setup 1 (above, no failures), and specimens tested with setup 2, 3 and 4. In these last three only three non-failures can be seen in setup 3 (circled in green)

During the measurements for setup 2 and 4, only failures were obtained. So, to double check if the problem was something related to the sample sheet and not the parameters, some variations to these setups were made on specimens obtained from the same sheets. For setup 2 different test speeds were tried keeping constant the other parameters. The test speeds tried were, in order: 100 mm/min (coinciding with parameters of set 2), 10 mm/min (coinciding of parameters of set 1), 40 mm/min and 20 mm/min. The picture of the specimen at the end of the tests is shown in the following figure.

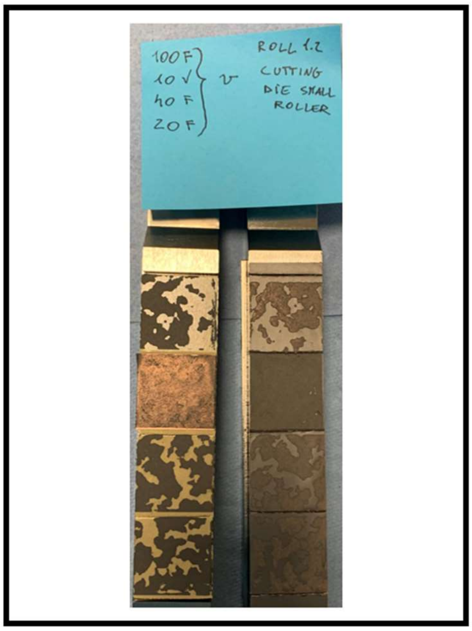


Figure 4.29 Specimens after testing at different testing speeds keeping the other parameters constant (setup 2)

As can be observed the only non-failure was obtained with the 10 mm/min speed, meaning using the parameters of setup 1.

For setup 4, one strip from the same sheet was tested using the parameters of setup 1.

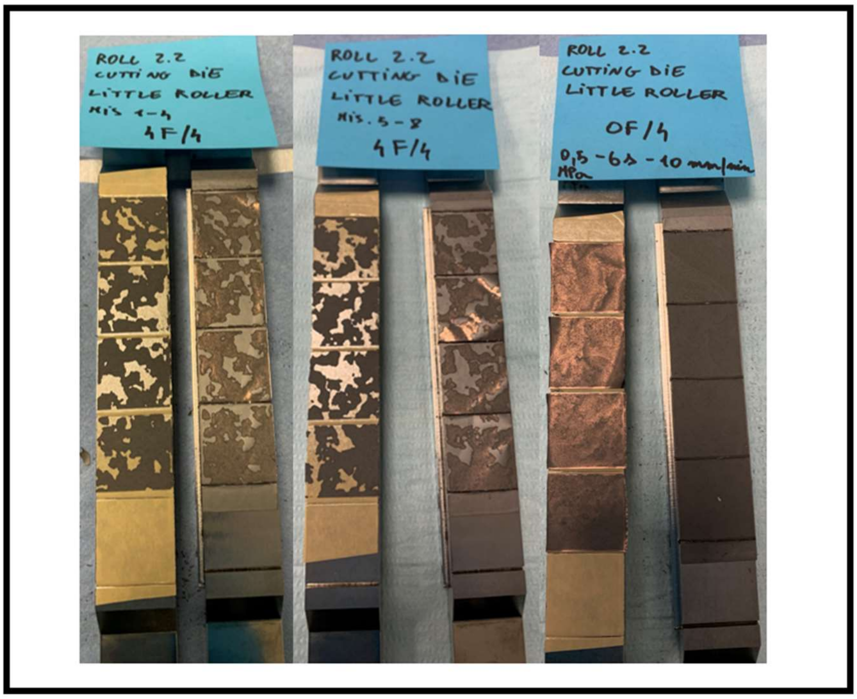


Figure 4.30 Specimens after testing with parameters of setup 4 (left and central) and with parameters of setup 1 (right)

As can be observed, testing with parameters of setup 1 led to zero failures.

Conclusions on effect of measurement testing parameters:

- The recommended parameters for the z-direction pull test of pressed anode sheets are the ones used in the first set of measurements (setup 1), described in table 4.12.
- No other tested parameters setups led to a sufficient number of non-failures.

4.3.5 Effect of adhesive tape type

To understand if there is an influence of the tape on the measurements, a second type of tape was used (Tesa®). For the specimen preparation, method 1 and method 2 were tried. For the parameters, setups 1 and 4 were used and an additional setup (5) was tried. All the parameter setups are shown in the following table.

Table 4.14 Parameter setup 1, 4 and 5 tried with the Tesa tape

Param.	Setup 1	Setup 4	Setup 5
Compressive stress	0.5 MPa	0.6 MPa	0.6 MPa
Dwell time	6 s	30 s	6 s
Test speed	10 mm/min	100 mm/min	100 mm/min
Data acquisition rate	2 kHz	2 kHz	2 kHz

Parameter setup 1 was tried only on method 1, while for method 2 setups 1, 4 and 5 were tried. The pictures of the specimens after the test are shown in the following figures. The numerical results are shown in table 4.15.

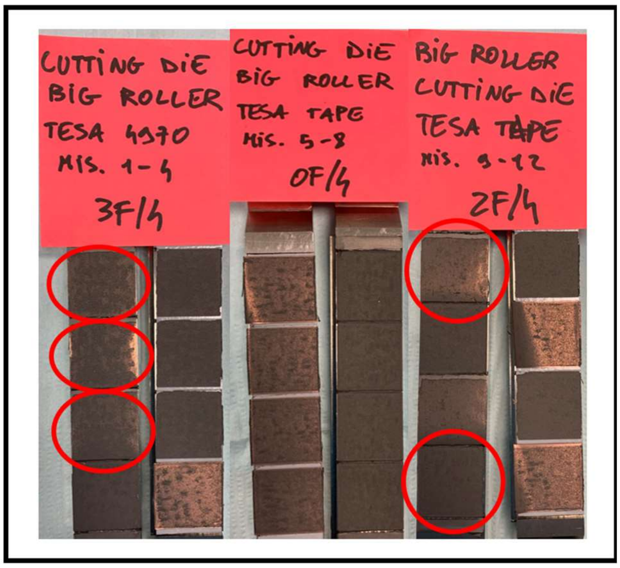


Figure 4.31 Specimens after testing with method 1 setup 1

Figure 4.32 Specimens after testing with method 2 setup 1

Figure 4.33 Specimens after testing with method 2 setup 4

Figure 4.34 Specimens after testing with method 2 setup 5

Table 4.15 Results of tests using the Tesa tape, failures are shown in brackets

	Method 1 Setup 1	Method 2 Setup 1	Method 2 Setup 4	Method 2 Setup 5
Max. tensile Force 1 [N]	(244.5)	(312.6)	406.8	415.8
Max. tensile Force 2 [N]	(251.4)	(301.4)	426.5	409.1
Max. tensile Force 3 [N]	(231.9)	(298.6)	425.9	(388)
Max. tensile Force 4 [N]	241.1	291.9	405.7	392
Max. tensile Force 5 [N]	252.3	(306.3)	407.5	412.6
Max. tensile Force 6 [N]	254.8	300.1	411.4	392.6
Max. tensile Force 7 [N]	262.7	297.4	416.6	(394.1)
Max. tensile Force 8 [N]	231.4	264.3	401.5	(396)
Max. tensile Force 9 [N]	(252.2)	(288.1)	428.9	422.3
Max. tensile Force 10 [N]	264.6	277	(419.3)	409.7
Max. tensile Force 11[N]	(239.2)	276.3	415.4	401.4
Max. tensile Force 12 [N]	238.7	278.9	395.7	(383)
Avg max. tensile force [N]	249.4	283.7	412.9	406.9
Sdev	12.6	13.1	10.8	10.8
Sdev%	5.1	4.6	2.6	2.7
Number of failures	5/12 (41.67%)	5/12 (41.67%)	1/12 (8.34%)	4/12 (33.33%)

Conclusions on the best specimen preparation and setup when using the Tesa tape:

- Setup 1 led to a high failure rate for both method 1 and method 2
- For setup 4 and 5 the avg max. tensile force is much higher than for setup 1. This is quite surprising; it might be due to the testing speed that is ten times higher for setup 4 and 5 compared to setup 1
- The lowest number of failures was obtained with method 2 setup 4
- The lowest standard deviation was obtained for method 2 setup 4 and 5
- When performing a z-direction pull test using the Tesa tape it is recommended to use method 2 setup 4

Comparison of 3M and Tesa tapes

Table.4.16 Results of tests using the best setups of each tape tried on both tapes, values for 3M method 2 setup 4 are shown in brackets because were all failures and these values are not taken into account for an effective comparison

	Tesa		3M	
	Method 2 Setup 1	**Method 2 Setup 4**	**Method 2 Setup 1**	**Method 2 Setup 4**
Avg max. tensile force [N]	283.7	412.9	151.7	(90.6)
Sdev	13.1	10.8	11.9	(14.4)
Sdev%	4.6	2.6	7.9	(15.9)
Number of failures	5/12 (41.67%)	1/12 (8.34%)	0/28	8/8 (100%)

Conclusions

- The best specimen preparation is method 2 for both tapes
- For the Tesa tape it is recommended to use setup 4
- For the 3M tape it is recommended to use setup 1
- The setup and the tape type affect the result
- The average maximum tensile force is very different in the two cases. The tape is affecting the results, but it is not well understood how. Further investigation should be carried out. A possible explanation is that a stronger tape (both stronger interface tape-grip and tape-Coat A) gives a more strained interface foil-coat A and therefore we are recording a higher value of the force. The problem is that we do not know the strength of the adhesion of the tape on the coating. We can record the adhesion between the grip and the tape, but not the one between the tape and the coating. We could assume that the tape with the higher adhesion to grip has also the higher adhesion to the coating, but since it is a very different material, we cannot be sure about this. In conclusion, the stronger tape should give a stronger value of the force, but we cannot record the adhesion strength between the coating and the tape.

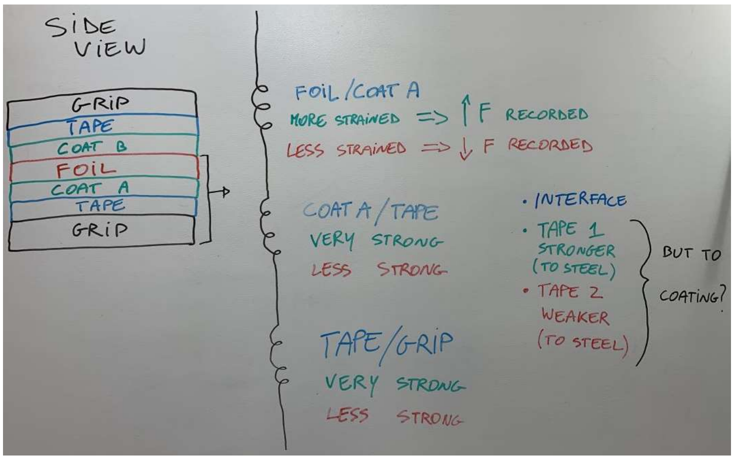


Figure 4.35 Representation of the possible explanation of how the tape is affecting the measurement

Investigation of the adhesion of both tapes to the grip

To find out the adhesion force of both tapes, some z-direction pull tests were performed. In these tests the double-sided tape was stuck only on one grip and no electrode was put in between the grips or stuck to the taped grip. In this way the adhesion of the tape to the grip was recorded. Both tapes were investigated with both setups 1 and 4. A schematic representation is presented in fig. 4.36.

Figure 4.36 Representation of the z-direction pull test to record the adhesion between the tape and the grip

Table 4.17 Recorded adhesion between tape and grip

	3M		Tesa	
	Setup 1	**Setup 4**	**Setup 1**	**Setup 4**
Max. tensile Force 1 [N]	258.4	641.4	459.2	1070.8
Max. tensile Force 2 [N]	268.5	585.6	454.4	1163.6
Max. tensile Force 3 [N]	279	614.3	480.6	1158.8
Max. tensile Force 4 [N]	284.3	595.9	472.7	1126.9
Max. tensile Force 5 [N]	271.7	580.3	458.8	-
Avg max tensile Force [N]	272.4	603.5	465.1	1130.1
Sdev	10.0	24.9	11.0	42.7
Sdev%	3.7	4.1	2.4	3.9

As can be noticed from the values shown in the table both the setup and the tape type (brand) affect the final result. Table 4.18 shows the ratio of the two tapes with both setups and the ratio of the two setups for both tapes.

Table 4.18 Ratio of both tapes and both setups

	Setup1	**Setup4**
Ratio 3M/Tesa	0.585587	0.534059
	3M	**Tesa**
Ratio setup1/4	0.451334	0.411619

So, the 3M tape has an adhesion force to steel between the 53-58% of the value of the Tesa tape so a bit more than the half. While the values recorded with setup 1 are between the 41-45% of the values recorded with the Tesa tape, so less than the half.

Table 4.19 Comparison of different adhesion values

	3M		Tesa	
	Setup 1	**Setup 4**	**Setup 1**	**Setup 4**
Avg F max tape-grip [N]	272.4	603.5	465.1	1130.1
Avg F max electrode [N]	151.7	-	283.7	412.9
Difference [N]	120.6	-	181.4	717.1
Difference%	28.4	-	24.2	46.5

The value tape-grip very distant from being the adhesion of the electrode. We can conclude that we are not measuring the adhesion of the tape, but effectively the adhesion of the electrode, even if it is affected by the tape type and the parameters used.

4.3.6 Effect on coated or uncoated specimens with both tapes

To understand if the coating is affecting the measurements tests on both coated and uncoated specimens were performed for both the Tesa and 3M tape. The tests were performed using specimens from sheets of the same roll. The best setup was used for each tape: setup 1 for 3M, setup 4 for Tesa. The results are shown in the following table.

Table 4.20 Results of tests using the best setups of each tape tried on both coated/uncoated specimens

	Tesa (Method 2 Setup 4)		**3M** (Method 2 Setup 1)	
	Coated	**Uncoated**	**Coated**	**Uncoated**
Max. tensile force 1 [N]	437.6	398.6	171.0	169.5
Max. tensile force 2 [N]	421.5	370.5	185.0	173.0
Max. tensile force 3 [N]	412.5	368.6	199.1	158.0
Max. tensile force 4 [N]	445.5	410.2	169.6	170.0
Max. tensile force 5 [N]	463.5	380.1	174.4	164.0
Max. tensile force 6 [N]	-	343.1	(181.3) F	-
Avg max. tensile force [N]	436.1	378.5	179.9	166.9
Sdev	23.8	20.1	12.4	5.9
Sdev%	5.4	5.3	6.9	3.6
Number of failures	0/5	0/6	1/6	0/5

Figure 4.37 Specimens tested with the Tesa tape, coated (left) and uncoated (right)

Figure 4.38 Specimens tested with the 3M tape, coated (left) and uncoated (right)

Conclusions:

- The coating removal was much more homogeneous for the uncoated specimens than for the coated ones when using the 3M tape. This effect is not observed when using the Tesa tape.
- For the Tesa tape the coating seems to affect the measurement (436 vs 378 N)
- For the 3M the coating does not seem to affect the measurement too much (179.9 vs 166.9). Although, when removing the coating the obtained standard deviation was very low. Further investigations on a larger amount of data should be done.

4.4 Conclusions on method development

The next step of the project is to perform the measurement system analysis (MSA) for each method to validate the test method and have a comparison between the tests.

For the 90° peel test, uncoated specimens are going to be tested using the 3M tape. Although, an MSA on coated specimens should be also performed to have a good comparison between the two methods.

For the z-direction pull test the MSA should be performed using the "method 2 setup 1" for the 3M tape. Also, an MSA using the Tesa tape should be performed, this time using "method 2 setup 4".

5. Measurement System Analysis (MSA)

5.1 Introduction to MSA

Measurement systems can produce unreliable data leading to bad decisions. Therefore, the measurement system must be determined as reliable before making decisions based on data recorded with that system. [58]

Data can be classified in two categories:

- Continuous (variable) data: quantitative data, they give a lot of information. it's basically anything we can measure. They can be described numerically or graphically.
- Discrete (attribute data): qualitative data, things we can count. [58]

We will focus on continuous/variable data. For these data the measurement system is comprised of the units being measured, the gauge, the operators and their methods.

A **measurement system analysis (MSA)** is a critical tool used to determine if the measurement system is a significant source of variability or not, its main purpose is to assess the quality of a measurement system. A MSA is a series of tests that, using the Analysis of Variance (ANOVA) evaluation method, allow to determine whether its measurement system is reliable in terms of:

- **Bias**: it is the difference between the observed average value of the measurements and a known standard value.
- **Linearity**: determines whether a bias exists in the measurement system over its operating range.
- **Stability**: determines the measurement system's ability to measure consistently over time such that the measurements system does not drift.
- **Discrimination**: it is the ability to detect small changes in the characteristic being measured.
- **Variability or precision**:
    - **Repeatability**: it is the ability of the measurement system to return the same measured value when one operator takes repeated measurements of the same unit. So, it is the variation that is observed when the same operator measures the same part many times, using the same gage, under the same conditions.
      Example: one operator measures a single part with Gage A 20 times, and then the same part 20 times with Gage B. [58] [59]

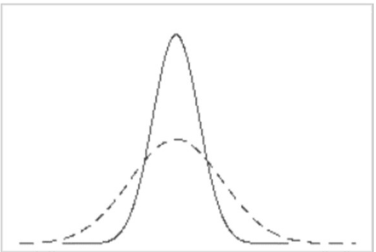


Figure 5.1 Measurement curves for Gage A and B

The continuous line is the measurement from gage A, the dashed one From Gage B. So, gage A has less variation and should therefore be preferred as measurement system.

-
    - **Reproducibility**: it is the variation observed when multiple operators measure the same characteristic on the same unit using the same Gage and in the same conditions. It's the variation due to the measurement system. [58]

Sources of process variation

- Part-to-part variation: it is the variability in measurements across different parts. Ideally, differences between parts (Part-to-Part) should be the highest source of variability.
- Measurement system variation: the measurement system variation is all the variation associated with a measurement process. Potential sources of variation include gages, standards, procedures, software, environmental components, etc. [60]

MSA components of variation

Any measurement of a part not only measures the true part value, but also measures any variability that may exist because of the poor repeatability of the gauge and/or the poor reproducibility of the operators and their methods of measuring. [58]

Gauge Repeatability and Reproducibility (GR&R) test

The GR&R test is a test that can be conducted to determine whether excessive variability exists in the measurements system. It is designed such that the product variability and the measurement system variability (also known as error or precision, p) can be partitioned from the total variability.

Total variability = product variability + measurement system variability

Measurement system variability = repeatability + reproducibility

Measurement system repeatability: it is the ability of one operator to measure one part multiple times without variability. [58]

Measurement system reproducibility: it is the ability of multiple operators to produce similar average measures for multiple parts, with minimal variability. Reproducibility can be split into two sources:

- Operator: The variability in measurements due to different operators.
- Operator-by-Part: The variability in measurements due to different operator/part combinations after considering part and operator separately. [60]

How to do a continuous GR&R test for destructive systems?

1. Identify the characteristic on the unit to be measured, the gauge and the operators.
2. Identify a certain number of units, this may require samples to be collected over several days or weeks. Split the parts into portions if possible and applicable for subjected measurement system or select parts/specimens from same batch/lot which is homogeneous and it is reasonable to say that they will act alike same parts. These criteria and assumptions are very critical because during R&R study, repeatability of the system will be assessed by using the variation between those specimens/samples from same batch and/or split part. Homogeneity of those batches/lots is always a question for this type of study so the results of statistical analysis will be never same with non-destructive test repeatability behaviour.

3. Conduct the GR&R in the environment where the measurement normally takes place
4. Estimate repeatability and reproducibility by conducting a test using, for example, three operators and the amount of samples determined by the nested or crossed MSA.
5. Calculate the variances using the ANOVA method: many different software packages can be used, for this project Minitab[2] is used.
6. Interpret the results graphically and analytically to determine whether the measurement system is acceptable, needs changes or must be replaced. [58]

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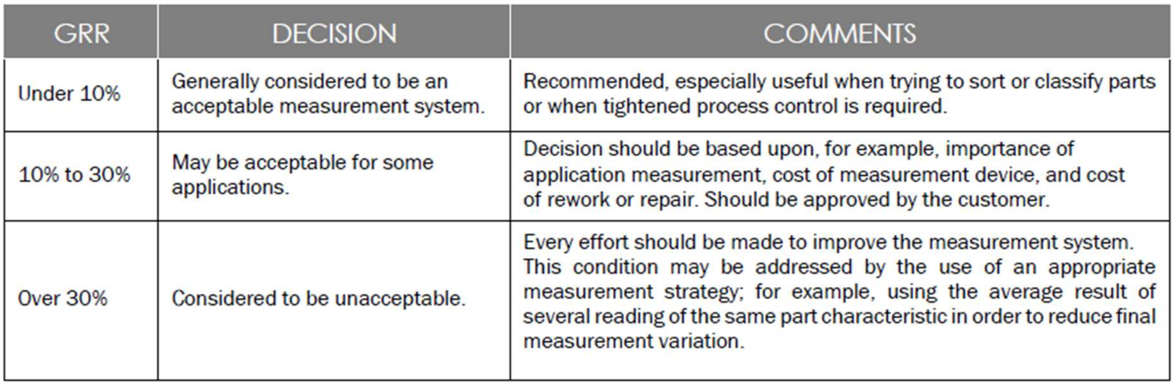
[2] Software specialized in statistical studies, heavily used in the industrial world.

Gauge R&R acceptance criteria

- % Tolerance: it is the variability of the measurement system compared to the tolerance range. [58]

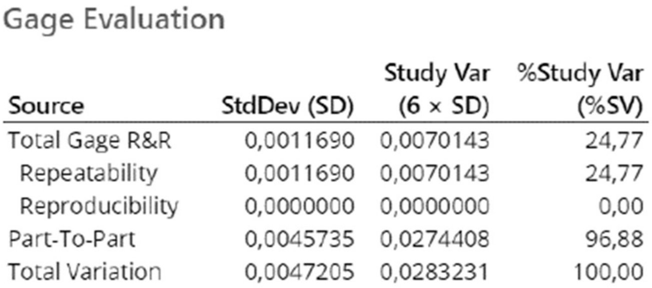
The guidelines for GR&R studies were defined originally by Automotive Industry Action Group (AIAG)[3] back in the 1990s. In GR&R, study variation (Study Var) is the amount of variation caused by the measurement system and by the differences between parts. It is calculated as 6 * the standard deviations of each source of variation. Minitab also calculates the percent study variation (%Study Var), so that you can compare the contribution of each component to the total variation. The acceptance criteria are defined in the following table. [61]

Table 5.1 GR&R acceptance criteria for % of Study of Variance [62]



GRR	DECISION	COMMENTS
Under 10%	Generally considered to be an acceptable measurement system.	Recommended, especially useful when trying to sort or classify parts or when tightened process control is required.
10% to 30%	May be acceptable for some applications.	Decision should be based upon, for example, importance of application measurement, cost of measurement device, and cost of rework or repair. Should be approved by the customer.
Over 30%	Considered to be unacceptable.	Every effort should be made to improve the measurement system. This condition may be addressed by the use of an appropriate measurement strategy; for example, using the average result of several reading of the same part characteristic in order to reduce final measurement variation.

Table 5.2 Example of results using Minitab



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Gage Evaluation

                                  Study Var  %Study Var
Source             StdDev (SD)     (6 × SD)       (%SV)
Total Gage R&R       0,0011690    0,0070143       24,77
  Repeatability      0,0011690    0,0070143       24,77
  Reproducibility    0,0000000    0,0000000        0,00
Part-To-Part         0,0045735    0,0274408       96,88
Total Variation      0,0047205    0,0283231      100,00
```

When it comes to %Contribution of Variance Components, this is referring to how much does each part contribute to the total variation seen in my study (We want most of it to come from the Part-to-Part Variation), they also have recommendations, when it comes to Total Gage R&R:

- <1%: acceptable no need for further improvements
- 1% - 9%: acceptable but accepting it will depend on the cost of the measuring device, cost of repair, etc. (We will call this, accept yet can be improved).
- >9%: improve, cannot trust the data

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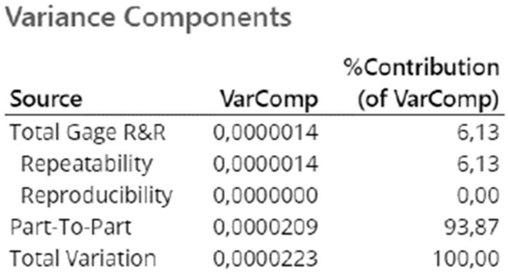
[3] The AIAG is a global organization that provides an open forum for companies from around the world to develop and share information that contributes to the automotive industry.

Table 5.3 Example of results from Minitab



Variance Components

Source	VarComp	%Contribution (of VarComp)
Total Gage R&R	0,0000014	6,13
Repeatability	0,0000014	6,13
Reproducibility	0,0000000	0,00
Part-To-Part	0,0000209	93,87
Total Variation	0,0000223	100,00

The AIAG also states that the number of distinct categories into which the measurement system divides process output should be greater than or equal to 5. “The number of distinct categories is a metric that is used in gage R&R studies to identify a measurement system's ability to detect a difference in the measured characteristic. The number of distinct categories represents the number of non-overlapping confidence intervals that span the range of product variation”. [63]

Crossed gage R&R study

In a crossed study, each operator measures each part. This study is called crossed because the same parts are measured by each operator multiple times.

Often, the crossed gage R&R study is used to determine how much of your process variation is due to measurement system variation. [64]

Two test specimens for each roll/batch are the minimum, for a total minimum of 10 tests per operator, 30 in total (3 operators). Operators measure specimens all from the same 5 batches.

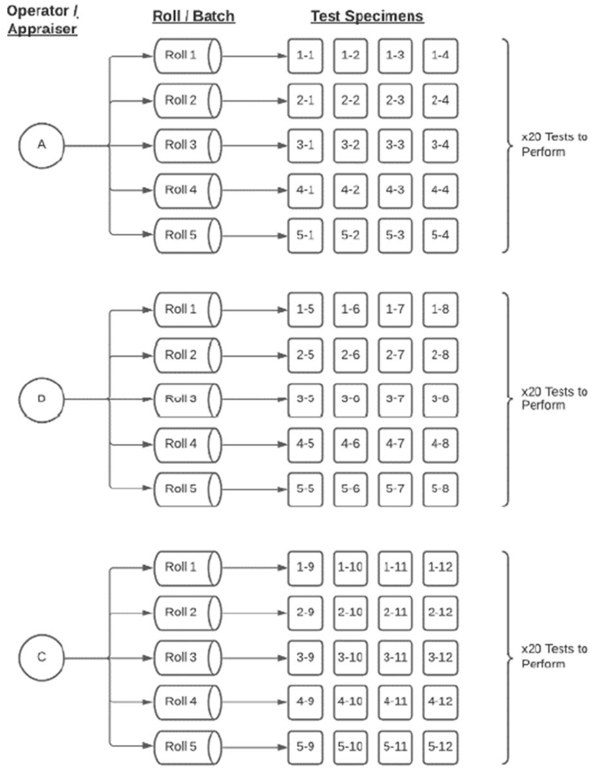


Figure 5.2 Crossed R&R study scheme

Nested gage R&R study

In a nested study, each part is unique to the operator; operators do not measure the same part. [64]

As for the crossed study, two test specimen for each roll/batch is the minimum, for a total minimum of 10 tests per operator, 30 in total (3 operators). Operators measure specimens all from different batches, therefore 15 batches are required (5 each).

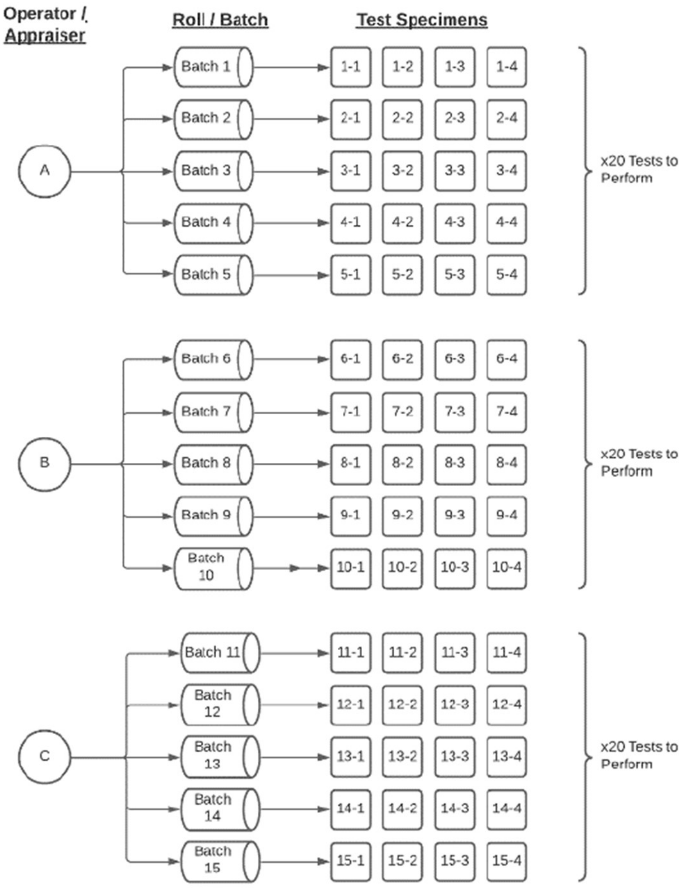


Figure 5.3 Nested R&R study scheme

If you use destructive testing during a gage R&R study, you must be able to assume that all parts within a single batch are identical enough to claim that they are the same part. If you are unable to make that assumption, then part-to-part variation within a batch will mask the measurement system variation.

If you can make that assumption, then your choice of using a crossed or a nested study for destructive testing depends on your measurement process. If all operators measure parts from each batch, use a crossed or expanded study. If each batch is measured by only one operator, use a nested or expanded study. Whenever operators measure unique parts, you have a nested design.

5.2 First set of MSA experiments

In the first set of MSA experiments, the Nested system was followed. Pressed anode sheets from 15 different rolls were collected and stored in the clean and dry room. Three operators performed the tests: each operator tested two specimens per roll for 5 different rolls, for a total of ten specimens per operator (30 measurements in total).

Three different MSAs were performed: 90° peel test uncoated, 90° peel test coated and 180° peel test uncoated.

5.2.1 90° peel test uncoated

The first MSA was performed for the 90° peel test with uncoated specimens. The results of the measurements are shown in table 5.4 and were put in Minitab under the Nested ANOVA study.

Table 5.4 Adhesion force recorded by each operator

Part	Operator	Result [N]	Sdev	Part	Operator	Result [N]	Sdev	Part	Operator	Result [N]	Sdev
1	Op.1	0.107	0.002	6	Op.2	0.100	0.002	11	Op.3	0.103	0.002
1	Op.1	0.103	0.002	6	Op.2	0.107	0.004	11	Op.3	0.103	0.002
2	Op.1	0.095	0.002	7	Op.2	0.077	0.002	12	Op.3	0.103	0.002
2	Op.1	0.105	0.002	7	Op.2	0.089	0.004	12	Op.3	0.102	0.002
3	Op.1	0.110	0.002	8	Op.2	0.078	0.002	13	Op.3	0.097	0.002
3	Op.1	0.109	0.003	8	Op.2	0.076	0.002	13	Op.3	0.097	0.002
4	Op.1	0.110	0.002	9	Op.2	0.078	0.002	14	Op.3	0.111	0.002
4	Op.1	0.110	0.002	9	Op.2	0.076	0.001	14	Op.3	0.110	0.002
5	Op.1	0.103	0.002	10	Op.2	0.078	0.002	15	Op.3	0.093	0.002
5	Op.1	0.106	0.002	10	Op.2	0.082	0.002	15	Op.3	0.097	0.002
Avg		0.1058	0.0021			0.0841	0.0023			0.1016	0.002
Sdev		0.0047				0.011				0.0058	

Table 5.5 Results from Minitab

Variance components		
Source	**VarComp**	**%Contribution (of VarComp)**
Total Gage R&R	0,0001312	71,28
Repeatability	0,0000118	6,41
Reproducibility	0,0001194	64,87
Part-To-Part	0,0000529	28,72
Total Variation	0,0001841	100,00

Table 5.6 Results from Minitab

Gage evaluation			
Source	**StdDev (SD)**	**Study Var (6 × SD)**	**%Study Var (%SV)**
Total Gage R&R	0,0114545	0,0687269	84,43
Repeatability	0,0034351	0,0206107	25,32
Reproducibility	0,0109273	0,0655636	80,54
Part-To-Part	0,0072715	0,0436291	53,59
Total Variation	0,0135676	0,0814057	100,00
Number of Distinct Categories = 1			

According to this study, the measurement system is not acceptable. Total Gage R&R %SV shows 84,43% (must be below 30% according to Northvolt Standards).

Most of the variability in this study is coming from Reproducibility, meaning there was a significant difference when placing different people to do this study.

Number of distinct categories is low, should be bigger than 5.

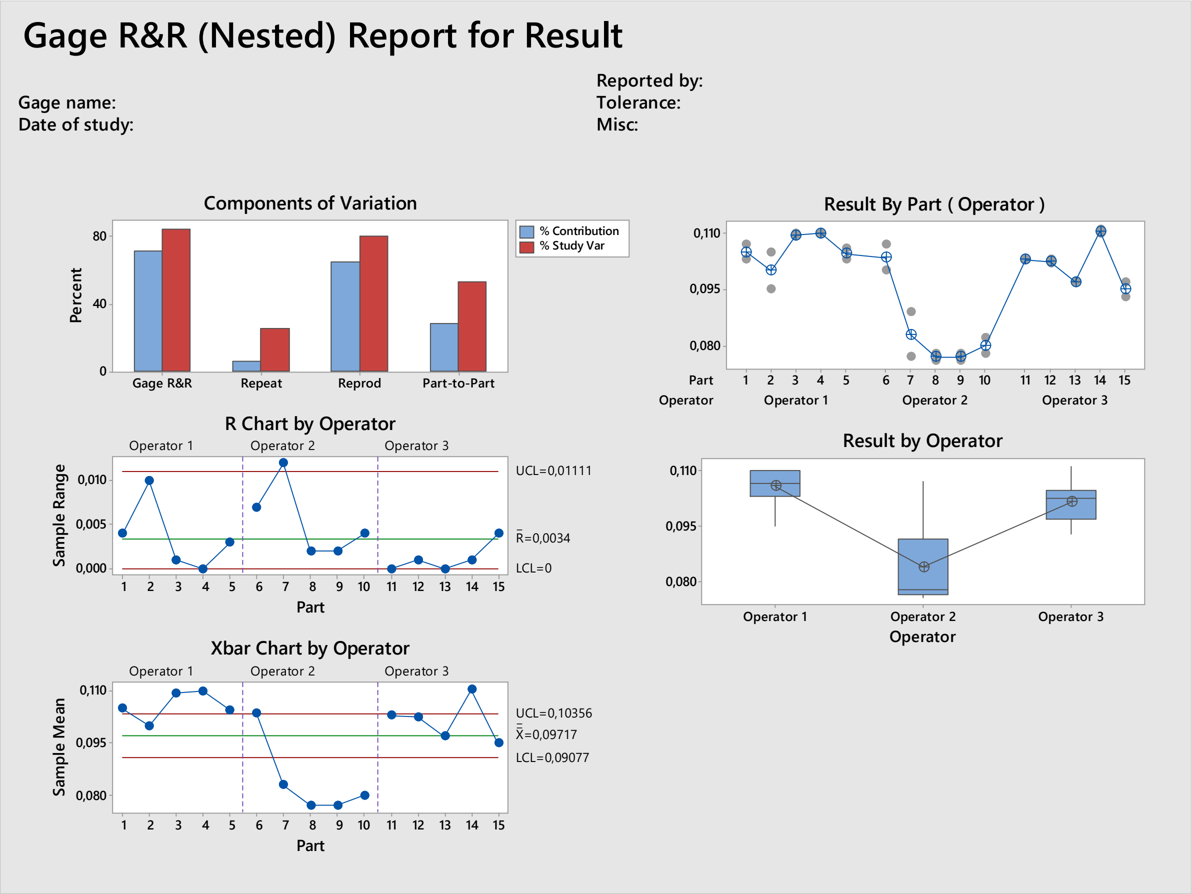


Figure 5.4 Gage R&R Nested report from Minitab for the uncoated 90° peel test MSA

What is each graph telling us? And what is visual expectation of each graph?

- On the “Components of Variation” bar chart, % Contribution, %StudyVar can be visualized.
- For “R Chart by Operator”, all points should be within the Control Limits. This shows that all operators can take consistent measurements. In case of out of control points are present, the root cause should be investigated
- For the “Xbar Chart by Operator”, many points should be out of the control limits. This shows that the variation within part is higher than the gage variability requested.
- For “Result By Part (Operator)” graph, individual points should be as close as possible. This shows low measurement system variability and it can also help to visualize that the system covers the tolerance range with different measurement means, which is also desired.
- For the “Measurement by Operator” graph, the expected behaviour is a horizontal straight line and close variation behaviour within operator box plots.

What we can see from these graphs is that operator 3 and the operator 1 are very similar in results, Operator 2 is showing the biggest inconsistencies.

Since four rolls given to operator 2 had a very low adhesion compared to all the other rolls and came from the same coating line but with a roll number quite distant from the others, the decision to take four new rolls and repeat those four measurements was taken. The results are shown in the following table.

Table 5.7 Results from each operator

Part	Operator	Force [N]	Sdev	Part	Operator	Force [N]	Sdev	Part	Operator	Force [N]	Sdev
1	Op.1	0.107	0.002	6	Op.2	0.100	0.002	11	Op.3	0.103	0.002
1	Op.1	0.103	0.002	6	Op.2	0.107	0.004	11	Op.3	0.103	0.002
2	Op.1	0.095	0.002	7	Op.2	0.103	0.002	12	Op.3	0.103	0.002
2	Op.1	0.105	0.002	7	Op.2	0.103	0.002	12	Op.3	0.102	0.002
3	Op.1	0.110	0.002	8	Op.2	0.098	0.002	13	Op.3	0.097	0.002
3	Op.1	0.109	0.003	8	Op.2	0.104	0.003	13	Op.3	0.097	0.002
4	Op.1	0.110	0.002	9	Op.2	0.091	0.003	14	Op.3	0.111	0.002
4	Op.1	0.110	0.002	9	Op.2	0.087	0.003	14	Op.3	0.110	0.002
5	Op.1	0.103	0.002	10	Op.2	0.088	0.002	15	Op.3	0.093	0.002
5	Op.1	0.106	0.002	10	Op.2	0.088	0.003	15	Op.3	0.097	0.002
Avg [N] **Sdev**		0.1058 0.0047	0.0021			0.0969 0.0076	0.0026			0.1016 0.0058	0.002

As can be noticed, operator's 2 standard deviation is much lower compared to the previous measurements, even though still quite higher than the other two operators. Also, the average is higher compared to the previous measurements even though still lower compared to the other operators. The results, once again, were put in Minitab under the Nested ANOVA study.

Table 5.8 Results from Minitab

Variance components		
Source	**VarComp**	**%Contribution (of VarComp)**
Total Gage R&R	0,0000204	37,76
Repeatability	0,0000082	15,09
Reproducibility	0,0000123	22,67
Part-To-Part	0,0000337	62,24
Total Variation	0,0000541	100,00

Table 5.9 Results from Minitab

Gage evaluation			
Source	**StdDev (SD)**	**Study Var (6 × SD)**	**%Study Var (%SV)**
Total Gage R&R	0,0045207	0,0271242	61,45
Repeatability	0,0028577	0,0171464	38,85
Reproducibility	0,0035029	0,0210171	47,61
Part-To-Part	0,0058037	0,0348224	78,89

Total Variation	0,0073566	0,0441398	100,00
Number of Distinct Categories = 1			

The total Gage R&R was brought down from 84% to 61% but still not acceptable. According to this study, in fact, the measurement system is not acceptable since the total Gage R&R %SV shows 61,45% (must be below 30% according to Northvolt Standards). Most of the variability in this study is coming from Reproducibility but also a high number comes from repeatability, meaning we could find variation between appraisers, but also between runs. Moreover, the number of distinct categories is low, should be bigger than 5.

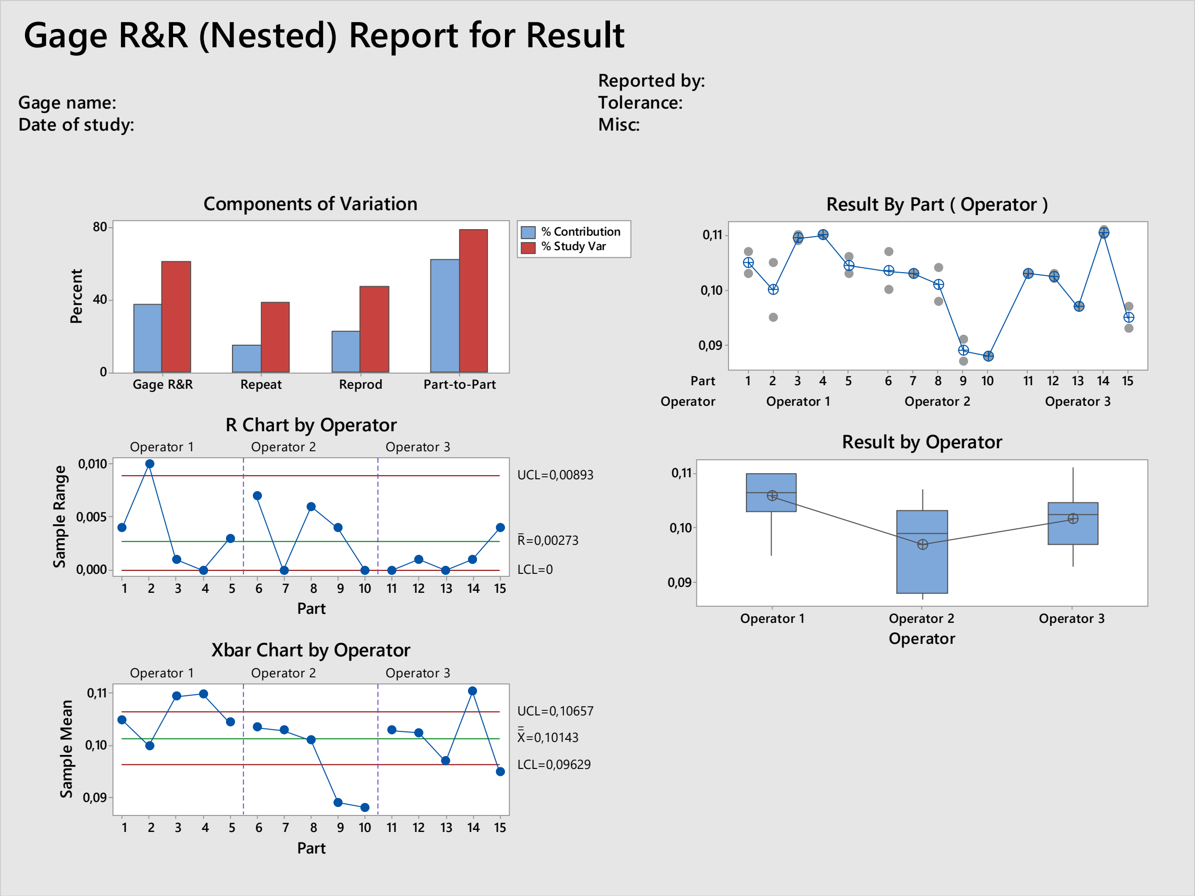


Figure 5.5 Gage R&R Nested report from Minitab for the uncoated 90° peel test MSA

Issues with Reproducibility are shown in the boxplot, operator 1 has a higher average than Op.3 and operator 2.

Differences within samples are also evident:

- In the case of Op.3, there is a consistent result for samples 11, 12, 13 and 14. 15 shows some difference, yet not something so significant.
- Operator 1 showed differences in samples 1, 2 and 5, with sample 2 being his biggest contributor.
- Operator 2 showed the biggest variability specified in samples 6, 8, 9, with 6 and 8 being her biggest contributors.

In order to further improve the results, it is recommended for the operators to double check the method and standardize practices. Moreover, it is important to check any external variables that could have affected the measuring device.

5.2.2 90° peel test coated

Even if during the method development the results suggested that the coating should be removed, an MSA study was conducted even on coated samples, to double check this and to have a good comparison between coated/uncoated specimens from the same rolls, tested from the same operators. A paragraph further on is dedicated to the comparison of the two methods and results.

Table 5.10 Results for the coated samples

Part	Operator	Result [N]	Sdev	Part	Operator	Result [N]	Sdev	Part	Operator	Result [N]	Sdev
1	Op.1	0.382	0.004	6	Op.2	0.358	0.004	11	Op.3	0.358	0.003
1	Op.1	0.405	0.003	6	Op.2	0.344	0.003	11	Op.3	0.358	0.004
2	Op.1	0.404	0.003	7	Op.2	0.341	0.003	12	Op.3	0.370	0.003
2	Op.1	0.386	0.003	7	Op.2	0.336	0.003	12	Op.3	0.364	0.003
3	Op.1	0.356	0.003	8	Op.2	0.323	0.004	13	Op.3	0.357	0.003
3	Op.1	0.354	0.003	8	Op.2	0.289	0.003	13	Op.3	0.349	0.003
4	Op.1	0.370	0.004	9	Op.2	0.308	0.003	14	Op.3	0.352	0.004
4	Op.1	0.370	0.006	9	Op.2	0.299	0.003	14	Op.3	0.352	0.004
5	Op.1	0.378	0.004	10	Op.2	0.300	0.004	15	Op.3	0.343	0.003
5	Op.1	0.355	0.003	10	Op.2	0.299	0.004	15	Op.3	0.343	0.004
Avg		0.376	0.0036			0.3197	0.0034			0.3546	0.0034
Sdev		0.0188				0.0238				0.0086	

The results were then put in Minitab under the Nested ANOVA study.

Table 5.11 Results from Minitab

Variance Components		
Source	**VarComp**	**%Contribution (of VarComp)**
Total Gage R&R	0,0008435	76,29
Repeatability	0,0000982	8,88
Reproducibility	0,0007454	67,41
Part-To-Part	0,0002622	23,71
Total Variation	0,0011057	100,00

Table 5.12 Results from Minitab

Gage Evaluation			
Source	**StdDev (SD)**	**Study Var (6 × SD)**	**%Study Var (%SV)**
Total Gage R&R	0,0290435	0,174261	87,34

Repeatability	0,0099079	0,059447	29,80
Reproducibility	0,0273013	0,163808	82,10
Part-To-Part	0,0161916	0,097149	48,69
Total Variation	0,0332520	0,199512	100,00
Number of Distinct Categories = 1			

According to this study, the measurement system is not acceptable. Total Gage R&R %SV shows 87,34% (must be below 30% according to Northvolt Standards). Most of the variability in this study is coming from Reproducibility, meaning there was a significant difference when placing different people to do this study. Moreover, the number of distinct categories is low, should be bigger than 5.

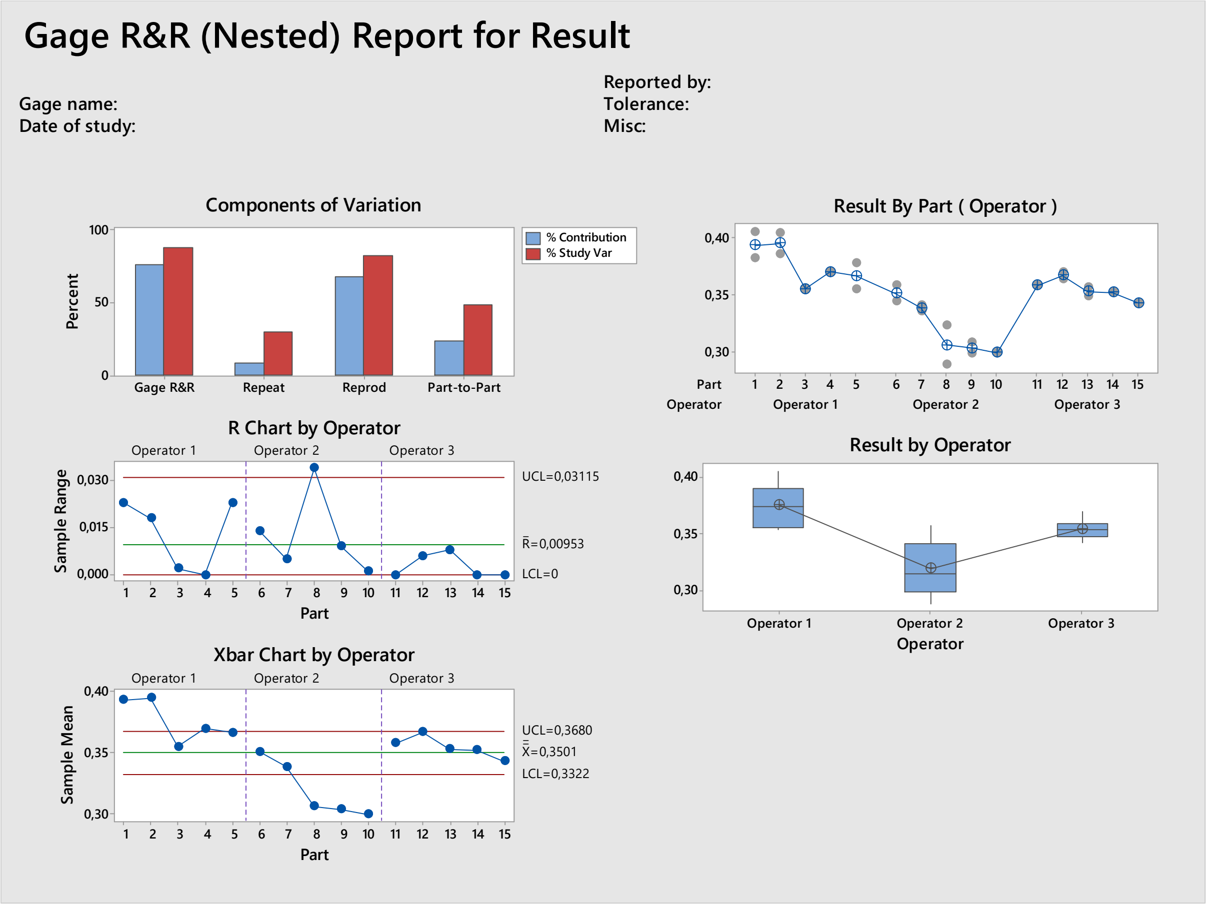


Figure 5.6 Gage R&R Nested report from Minitab for the coated 90° peel test MSA

Result by Operator shows significant differences between the measurements. Op.3 showed a lot of consistency, whereas operator 1 and operator 2 showed more variability and differences in their mean values. This is what affected the result in Reproducibility.

5.2.1 180° peel test uncoated

Even if the 180° peel test had already been validated, an MSA was performed to have a comparison with the 90° peel test when the same operators performed the tests on same rolls. The results are shown in the following table.

Table 5.13 Results from the 180° peel test MSA of uncoated specimens

Part	Operator	Result [N]	Sdev	Part	Operator	Result [N]	Sdev	Part	Operator	Result [N]	Sdev
1	Op.1	0.069	0.002	6	Op.2	0.066	0.002	11	Op.3	0.068	0.001
1	Op.1	0.075	0.002	6	Op.2	0.066	0.002	11	Op.3	0.068	0.002
2	Op.1	0.080	0.002	7	Op.2	0.063	0.001	12	Op.3	0.070	0.001
2	Op.1	0.075	0.002	7	Op.2	0.065	0.003	12	Op.3	0.068	0.002
3	Op.1	0.079	0.002	8	Op.2	0.070	0.001	13	Op.3	0.069	0.001
3	Op.1	0.086	0.002	8	Op.2	0.066	0.002	13	Op.3	0.069	0.001
4	Op.1	0.071	0.001	9	Op.2	0.057	0.001	14	Op.3	0.070	0.001
4	Op.1	0.068	0.001	9	Op.2	0.057	0.001	14	Op.3	0.068	0.001
5	Op.1	0.067	0.001	10	Op.2	0.055	0.001	15	Op.3	0.068	0.001
5	Op.1	0.067	0.001	10	Op.2	0.053	0.001	15	Op.3	0.064	0.001
Avg		0.0737	0.0016			0.0618	0.0015			0.0682	0.0012
Sdev		0.0064				0.0058				0.0017	

Table 5.14 Results from Minitab

Variance Components		
Source	**VarComp**	**%Contribution (of VarComp)**
Total Gage R&R	0,0000359	60,99
Repeatability	0,0000056	9,46
Reproducibility	0,0000303	51,53
Part-To-Part	0,0000230	39,01
Total Variation	0,0000588	100,00

Table 5.15 Results from Minitab

Gage Evaluation			
Source	**StdDev (SD)**	**Study Var (6 × SD)**	**%Study Var (%SV)**
Total Gage R&R	0,0059907	0,0359441	78,09
Repeatability	0,0023594	0,0141563	30,76
Reproducibility	0,0055065	0,0330391	71,78
Part-To-Part	0,0047915	0,0287489	62,46
Total Variation	0,0076712	0,0460269	100,00
Number of Distinct Categories = 1			

According to this study, the measurement system is not acceptable. Total Gage R&R %SV shows 78.09% (must be below 30% according to Northvolt Standards). Most of the variability in this study is coming from Reproducibility, meaning there was a significant difference when placing different people to do this study. Moreover, the number of distinct categories is low, should be bigger than 5.

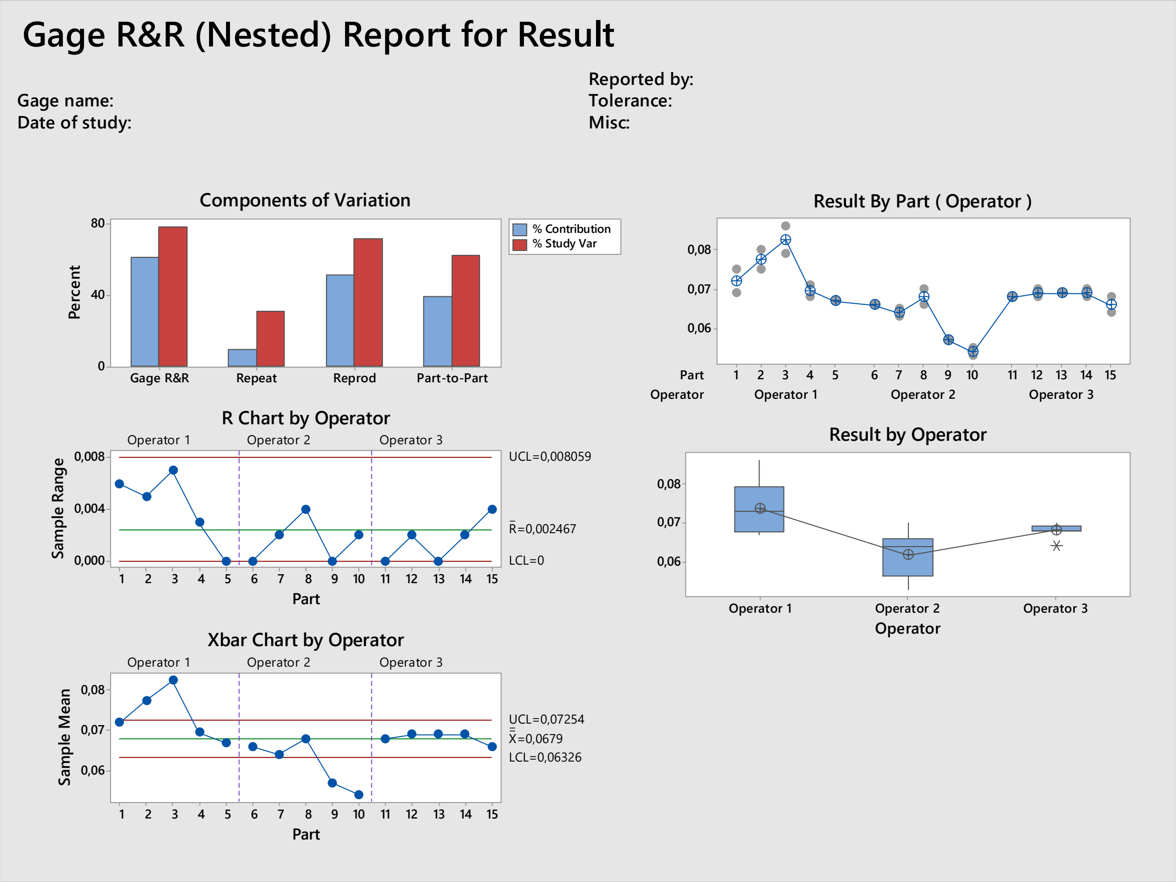


Figure 5.7 Gage R&R Nested report from Minitab for the 180° peel test MSA

Result by Operator shows significant differences between the measurements. Op.3 showed a lot of consistency, whereas operator 1 and 2 showed more variability. This is what affected the result in Reproducibility.

5.2.4 Comparison of the 90° coated/uncoated peel test

A comparison of the results between coated/uncoated specimens is carried out. Each operator has performed the tests on the same rolls for both specimen preparation (e.g. operator1 on roll 1, 2, 3, 4, 5; op.2 on 6, 7, 8, 9, 10). But operator 1 was a different person for the two tests.

Table 5.16 Comparison of results for all operators

	90° coated Adhesion Force [N]	90° coated Sdev range	90° uncoated Adhesion Force [N]	90° uncoated Sdev range	Difference in Adhesion Force [N]	Difference % in Adhesion Force
Op.3						
Avg	0.3546	0.0034	0.1016	0.002	0.253	55.46
Sdev	0.0086		0.0058			
Sdev%	2.43		5.70			
Op.1						
Avg	0.376	0.0036	0.1058	0.0021	0.270	56.08
Sdev	0.019		0.0047			
Sdev%	4.98		4.43			
Op.2						
Avg	0.3197	0.0034	0.0969	0.0026	0.2228	53.48
Sdev	0.0238		0.0076			
Sdev%	7.45		7.91			

Observations:

- The average value of the coated specimens is much higher compared to the uncoated specimens for all operators. This had already been noticed during the method development, and it is due to the much higher contribution from the bending when on the foil there is the coating. Higher energy is required to bend the coated foil compared to the bare foil, so the contribution is much higher resulting in a higher value recorded of the adhesion force.
- The values of the adhesion force are comparable for all operators for the uncoated specimens, while the coated specimens showed more variance. This can clearly be seen in the graph of fig 5.8 shown below.
- The standard deviation as a value is always lower for the uncoated specimens. Although, if the percentage value is considered, it is comparable for operator 1 and 2, while for Op.3 the uncoated value is two times the coated one, which is quite surprising.
- The standard deviation of the range (previously defined also as the natural variation of the process) is much lower for the uncoated specimens (more accurate values then).
- Operator 2 has the lowest difference in the average value of the adhesion force recorded for the two tests, operator 1 the highest, while Op.3 is in the middle. The difference % is similar for all operators.
- The measurement system was far away from being acceptable in both cases. The total Gage R&R was 61.45% and 87.34%, for the 90° peel test uncoated and coated respectively, when it should be below 30%.

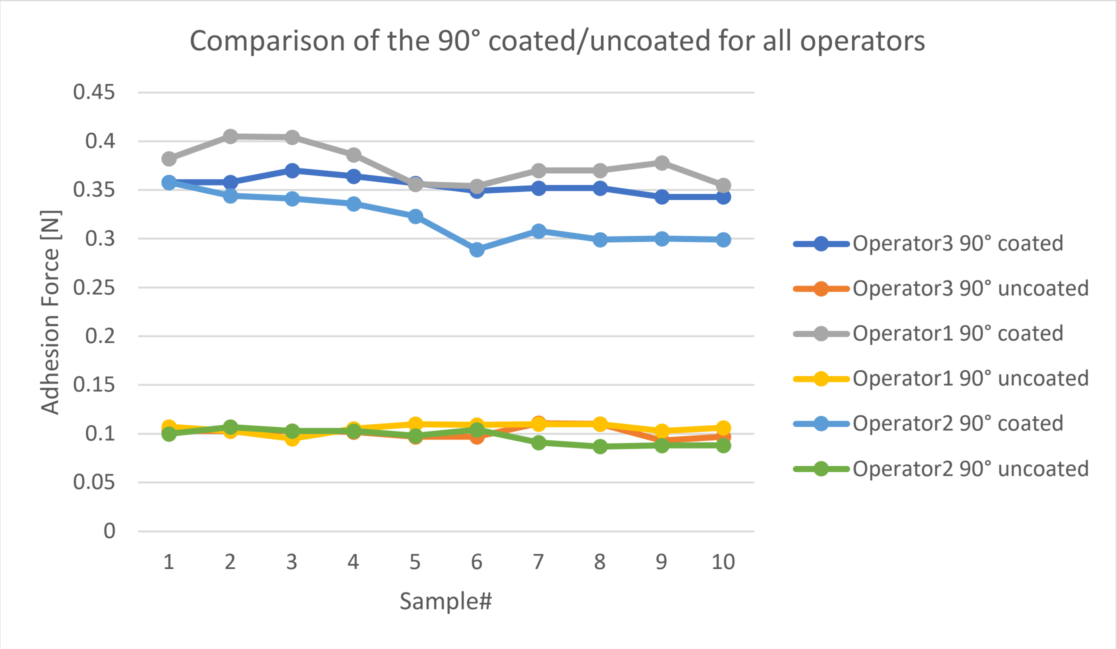


Figure 5.8 Comparison of the adhesion force for the 90° coated/uncoated peel test for all operators

5.2.5 Comparison 90°/180° peel test uncoated

A comparison of the results between 90°/180° peel tests on uncoated specimens is carried out. Each operator has performed both tests on the same rolls (e.g. operator1 on roll 1, 2, 3, 4, 5; op.2 on 6, 7, 8, 9, 10).

Table 5.17 Results of the 90°/180° peel tests for all the oparators

	180°Adhesion Force [N]	180° Sdev range	90°Adhesion Force [N]	90° Sdev range	Difference in Adhesion Force [N]	Difference % in Adhesion Force
Op.3						
Avg	0.0682	0.0012	0.1016	0.002	0.0334	19.67
Sdev	0.0017		0.0058			
Sdev%	2.47		5.70			
Op.1						
Avg	0.0737	0.0016	0.1058	0.0021	0.0321	17.88
Sdev	0.0064		0.0047			
Sdev%	8.75		4.43			
Op.2						
Avg	0.0618	0.0015	0.0969	0.0026	0.0351	22.11
Sdev	0.0058		0.0076			
Sdev%	9.37		7.91			

Observations:

- The measurement system was far away from being acceptable in both cases. The total Gage R&R was 61.45% and 78.09%, for the 90° and 180°peel test respectively, when it should be below 30%.

- The standard deviation of the range (previously defined also as the natural variation of the process) is lower for the 180° specimens (more accurate values then).
- The standard deviation of the adhesion force is lower for the 180° than for the 90° only for Op.3 for both the value and the percentage value. For operator 1 it is the contrary. For operator 2 the value is lower for the 180°, but it is higher as percentage value. This suggests that the two tests are comparable.
- The difference in adhesion force of the two tests is quite similar for all the operators
- The average value of the adhesion force is lower for all the operators for the 180° peel test. In literature it was suggested (already mentioned in chapter 3), that a higher angle would lead to a higher contribution from the bending of the foil. So, the 90° peel test was expected to give a cleaner measure and we recorded higher values on the 90°. We tried to highlight the forces acting in the two tests: in the 90° peel test we are measuring pure tensile (only tension, mode 1), while in the 180° peel test a contribution of tension (mode 1) and shear (mode 2) is recorded. We should then expect a higher value for the 180° because it is the sum of two contributions, but this is not true; the explanation could be that the coating is sensitive to shear and gives a negative contribution to the value recorded that is therefore going to be lower than the one recorded for the 90°. The following figure represents this argument.

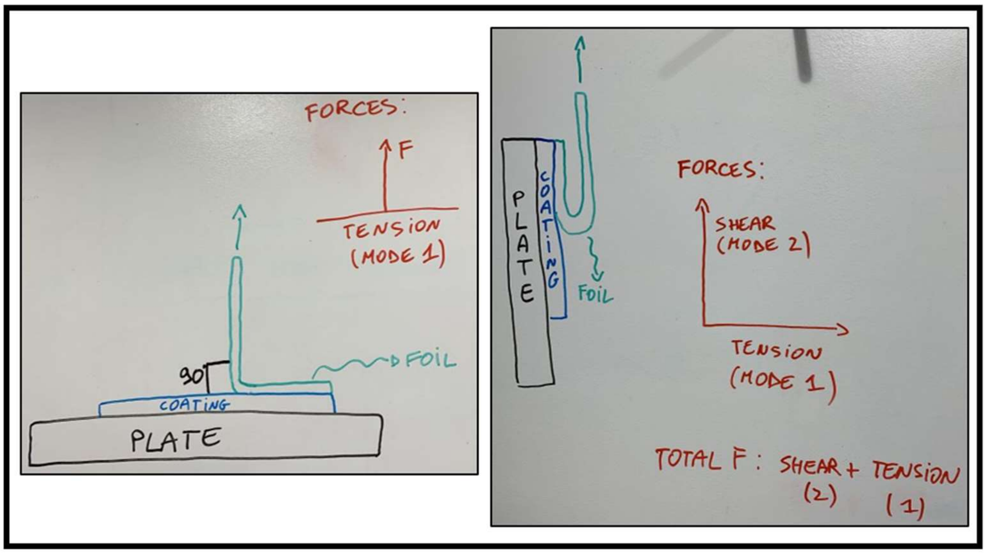


Figure 5.9 Representation of the two tests with the relative scheme of the forces acting

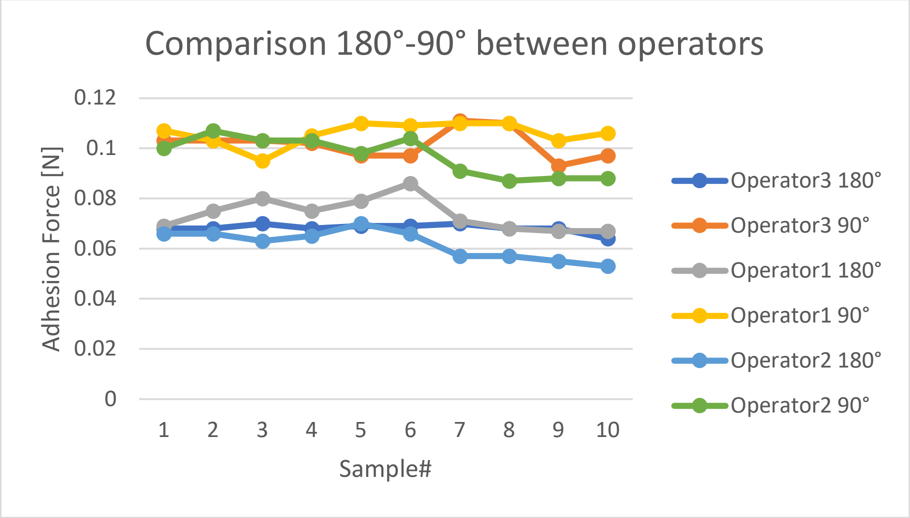


Figure 5.10 Comparison of the adhesion force for both tests for all the operators

5.2.6 Comparison of the values recorded of the three methods

Table 5.18 Average adhesion force values for all the tests for all the operators

	180°Adhesion Force [N]	90° uncoated Adhesion Force [N]	90° coated Adhesion Force [N]	Adhesion F difference 90° coated/uncoated [N]	Adhesion F difference 90°/180° [N]
Op.3					
Avg	0.0682	0.1016	0.3546	0.253	0.0334
Op.1					
Avg	0.0737	0.1058	0.376	0.270	0.0321
Op.2					
Avg	0.0618	0.0969	0.3197	0.2228	0.0351

Observations:

- Operator 1 has the highest values for all three tests. Operator 2 has the lowest values for all three tests. Op.3 has the intermediate values in all three tests. There are mainly two possible explanations to this trend:
    - Each operator has followed the same specimen preparation, although slight differences in the preparation might affect the final result. The specimen preparation is the only thing that all the three tests have in common.
    - Since the operators are testing always sheets from the same five rolls each (op.1: 1-5, op.2: 6-10, Op.3: 11-15), these rolls might have a slightly difference in adhesion. This is, hopefully, the explanation, also considering the fact that the operator 1 for the 90 peel test coated was not the same person of the other two tests, but however had the highest results once again.

  Two decisions were then taken:

    1. Run a meeting in which operators discuss in detail the method preparation, trying to find out possible differences that are affecting the results
    2. A new way of collecting the samples to test will be used for the following MSAs. In fact, since 15 rolls might be too inhomogeneous, only sheets from the same five rolls will be taken. This seems to be the Crossed gage R&R Study way of collecting samples, although the nested study is going to be run once again with the assumption that different sheets from the same rolls can be considered as different batches. Therefore, even if each operator is testing a sheet from the same roll, the total number of batches will be once again 15. This assumption is made because it is known (from tests prior to this project) that sheets are not homogeneous. Moreover, this assumption had already been made when the 180° peel test had been validated prior to this project.

5.3 Second set of MSA experiments

In this second set of experiments, only 5 rolls were used. Operators tested specimens obtained from different sheets of the same five rolls. The Nested program was however used in Minitab.

Due to lack of time, only two experiments were performed: the z-direction pull test using both the 3M and the Tesa tape.

5.3.1 Z-direction pull test using the 3M tape

As suggested from the method development, method 2 (to prepare the specimens) and setup1 were used.

Surprisingly, on the contrary of what achieved during the method development, a non-uniform coating removal was achieved. Moreover, the detachment occurred between the foil and the B side of the coating. Since this happened for each measurement done by each operator, the decision to bring off the study was taken and take conclusions at the end.

Table 5.19 Maximum tensile force recorded in Newton by each operator in the MSA study

Part	Operator	Result [N]	Part	Operator	Result [N]	Part	Operator	Result [N]
1	Operator1	159.4	6	Operator2	167.3	11	Operator3	156.6
1	Operator1	161	6	Operator2	170	11	Operator3	162.1
2	Operator1	135.2	7	Operator2	149.2	12	Operator3	176.1
2	Operator1	133.1	7	Operator2	155.8	12	Operator3	176.5
3	Operator1	165.4	8	Operator2	157.6	13	Operator3	170.1
3	Operator1	164.2	8	Operator2	157.4	13	Operator3	163.2
4	Operator1	153.6	9	Operator2	150.2	14	Operator3	152
4	Operator1	159.6	9	Operator2	149.6	14	Operator3	154.6
5	Operator1	159.3	10	Operator2	148.9	15	Operator3	155
5	Operator1	161.7	10	Operator2	154.6	15	Operator3	153.1

Table 5.20 Results from Minitab

Variance Components		
Source	**VarComp**	**%Contribution (of VarComp)**
Total Gage R&R	7,410	7,19
Repeatability	7,410	7,19
Reproducibility	0,000	0,00
Part-To-Part	95,635	92,81
Total Variation	103,045	100,00

Table 5.21 Results from Minitab

Gage Evaluation			
Source	**StdDev (SD)**	**Study Var (6 × SD)**	**%Study Var (%SV)**
Total Gage R&R	2,7221	16,3328	26,82
Repeatability	2,7221	16,3328	26,82
Reproducibility	0,0000	0,0000	0,00
Part-To-Part	9,7793	58,6759	96,34
Total Variation	10,1511	60,9066	100,00
Number of Distinct Categories = 5			

According to this study, the measurement system is acceptable. Total Gage R&R %SV shows 26.82% (must be below 30% according to Northvolt Standards). Most of the variability in this study is coming from Parto-To-Part as it should be. Reproducibility does not contribute, while quite a high number comes also from repeatability. The number of distinct categories is 5 which is acceptable.

A "bad detachment" of the samples was obtained (not what was found during the method development), but the measurement system showed good consistency. All the operators obtained a non-homogeneous detachment between the foil and the B side of the coating. The "bad detachment" should not be due to the measurement system since during the method development a "good detachment" was obtained in the same conditions, using the same measurement system and testing different sheets from different rolls. Therefore, there is need to investigate the cause of this different detachment.

In conclusion, the measurement system can be accepted with the condition to investigate why the detachment occurred in a non-homogeneous way between the foil and the B side of the coating. It is also suggested to try the measurement system again, testing new samples.

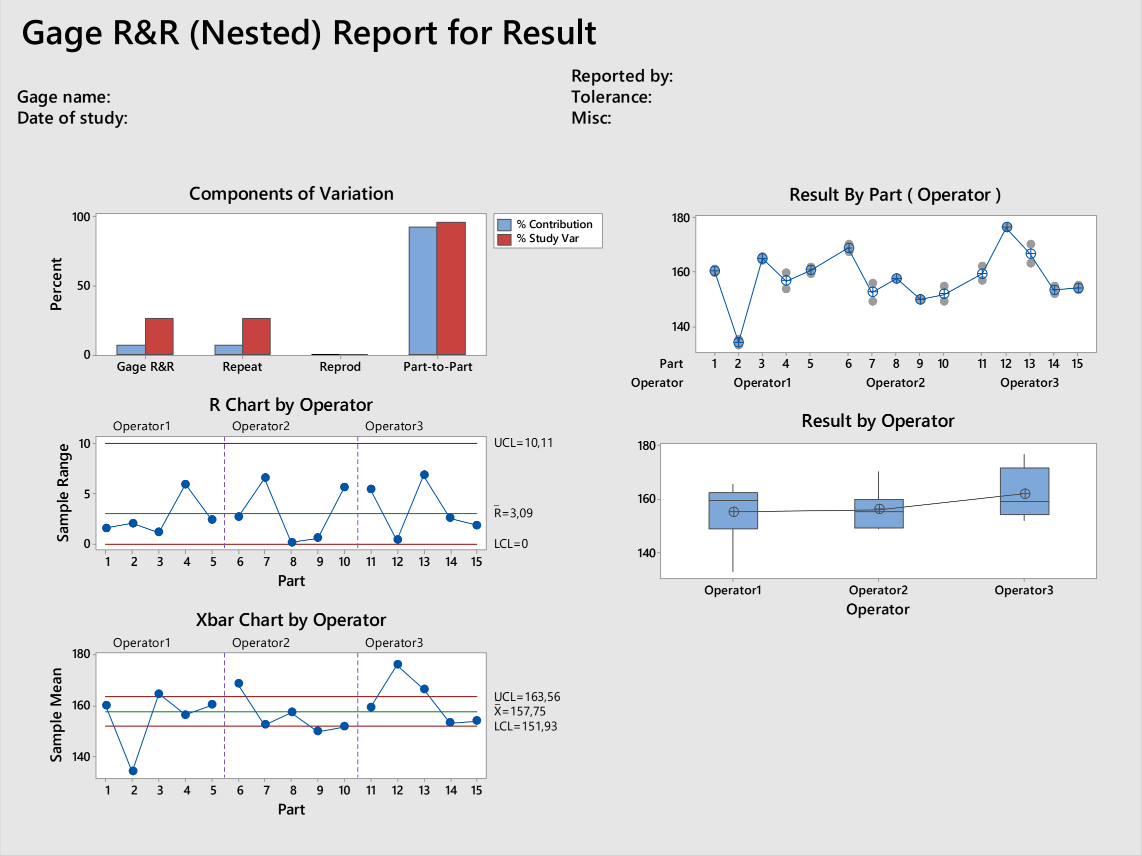


Figure 5.11 Gage R&R Nested report from Minitab for the z-direction pull test for the 3M tape

5.3.2 Z-direction pull test using the Tesa tape

As suggested from the method development, method 2 (to prepare the specimens) and setup4 were used.

Table 5.22 Maximum tensile force recorded in Newton by each operator in the MSA study

Part	Operator	Result [N]	Part	Operator	Result [N]	Part	Operator	Result [N]
1	Operator1	328.2	6	Operator2	328	11	Operator3	335
1	Operator1	333.4	6	Operator2	327.8	11	Operator3	325.4
2	Operator1	341.3	7	Operator2	343.4	12	Operator3	355.1
2	Operator1	336	7	Operator2	340.6	12	Operator3	355.9
3	Operator1	337.1	8	Operator2	306.7	13	Operator3	340.7
3	Operator1	328	8	Operator2	307	13	Operator3	340.1
4	Operator1	325	9	Operator2	328.6	14	Operator3	347.8
4	Operator1	328.8	9	Operator2	323	14	Operator3	347.2
5	Operator1	341.6	10	Operator2	315.9	15	Operator3	357.8
5	Operator1	341.9	10	Operator2	314.2	15	Operator3	357.1

Table 5.23 Results from Minitab

Variance Components		
Source	**VarComp**	**%Contribution (of VarComp)**
Total Gage R&R	115,775	51,54
Repeatability	9,623	4,28
Reproducibility	106,151	47,25
Part-To-Part	108,877	48,46
Total Variation	224,651	100,00

Table 5.24 Results from Minitab

Gage Evaluation			
Source	**StdDev (SD)**	**Study Var (6 × SD)**	**%Study Var (%SV)**
Total Gage R&R	10,7599	64,5592	71,79
Repeatability	3,1021	18,6129	20,70
Reproducibility	10,3030	61,8179	68,74
Part-To-Part	10,4344	62,6063	69,62
Total Variation	14,9884	89,9302	100,00
Number of Distinct Categories = 1			

According to this study, the measurement system is not acceptable. Total Gage R&R %SV shows 71.79% (must be below 30% according to Northvolt Standards). Most of the variability in this study is coming from Reproducibility. The number of distinct categories is 1 which is low.

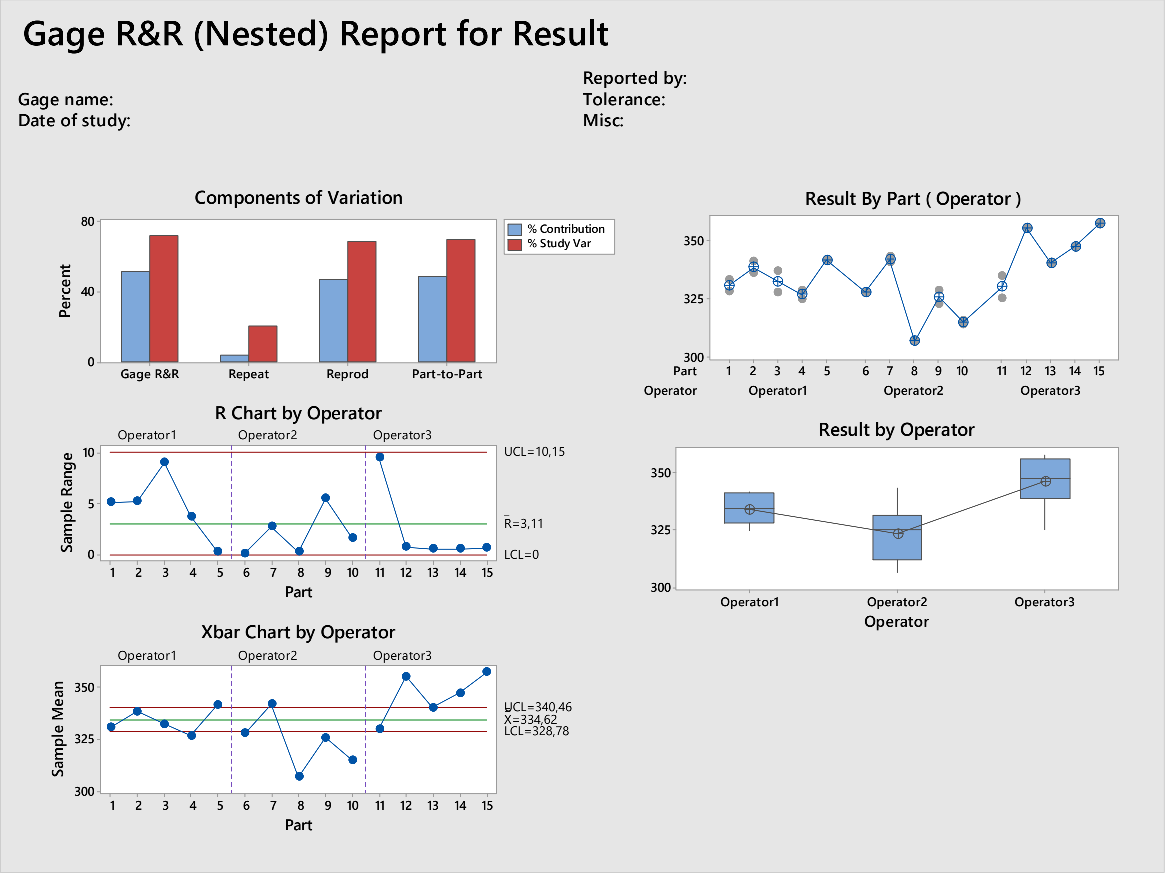


Figure 5.12 Gage R&R Nested report from Minitab for the z-direction pull test for the Tesa tape

6. Conclusions

Since the coating adhesion in a battery cell is one of the critical parameters to control to ensure long-lasting performance, there is need to find the best testing setup and develop a standard to measure the coating adhesion of the electrodes.

In this project, a method to test the coating adhesion of electrodes was developed using the 90°peel test and the z-pull test setup. Moreover, an attempt to validate and compare these two methods along with the 180°peel test was initiated following the guidelines of a measurement system analysis.

A limitation to consider in this investigation is that this project only tested dry electrode, while in operation, the electrode would be wet (soaked by the electrolyte present. Hence, the investigation has been done in conditions that are not mimicking the conditions of the electrode when the battery is in operation. At the state of the art, there is no test known that could reproduce the exact conditions of the battery cell during service. Furthermore, it is vital that the coating adhesion, being an important parameter, is controlled during the battery manufacturing process.

Conclusions from the method development:

- During sample preparation for the 90° peel test, the coating must be removed. Therefore, the specimen preparation for the 90° peel test and the 180° peel test are identical and require a lot of time.
- Since the 90° peel test is very similar to the 180° peel test, once validated, this test could be used for quality control inspection of electrode production samples. Although, according to the opinion of multiple operators, the 90° is more difficult to perform: the lower grip is heavier, putting the wire in place is not easy, and the foil is more difficult to clamp to the upper grip.
- The 90° peel test records higher peeling force values compared to the 180° peel test, when testing sheets from the same rolls. It has happened with three different operators. This is in accord with literature, that suggested a higher contribution from deformation for higher peeling angles (higher bending of the foil required). Therefore, it is possible to confirm that the 90° gives a "cleaner" measure.
- For the z-direction pull test, the setup and the tape affect the result. Tapes with a stronger adhesion are thought to give a higher value of the maximum tensile force, as explained in chapter 4.
- The z-direction pull test is quicker and easier than the other two tests, according to the opinion of multiple operators. It allows to test 5 different specimens for one sample preparation. The specimen removal process from the grip after testing has to be improved further, since it is the part requiring the most amount of time. Moreover, the main drawback is that the fixture is very heavy and difficult to put in place in the UTM. Since the tensile tester is used also for other types of tests, the fixtures/grips have to be changed multiple times, and this requires a bit of strength, so not all operators might be able to change it. A separate, dedicated UTM for this specific test should be used if implemented as a routine inspection.
- It is true that the z-direction peel test allows to test 5 different specimens, but the peel test records 4 values in a similar length of the sample.
- The peel test gives more information. The graph helps to see if there is "X, Y, Z" defect in the sample. There is no help in this way from the graph of the z-direction pull test. Moreover, the peel test gives a value of the standard deviation of the range, which is an indication of the reliability of the measurement.

Conclusions from the MSA studies

The nested study was chosen instead of the crossed one, because in the crossed study each operator measures the same part. Since we could not guarantee that each sheet from the same roll would have identical adhesion, the nested study was chosen. In this study each part is unique so, the operators are not measuring the same part.

However, the validation of the 90° peel test has not been successful using the ‘nested’ study. Since the MSA is done on destructive samples, at first, it was not well understood if the non-successful result was due to the method system, to the operators or to the inhomogeneity of the sheets tested. Although, it is known that the adhesion is not homogeneous in the width of a sheet, and it is not homogeneous in different sheets from the same roll, even along the same coating line. This means that two sheets from the same roll could be considered as two different batches. With this assumption, a new MSA study has been performed taking different sheets from the same five rolls for all the three operators (following the ‘crossed’ study sample collection), but running the ‘nested’ program.

Due to time limitations in this project, this new MSA approach has only been performed on the z-direction pull test, but for both tapes (3M and Tesa). The study has been successful for the 3M tape but not for the Tesa. This means that:

- the z-direction pull test using “method 2 – setup 1” with the 3M tape has been successfully validated.
- the non-successes of the previous MSA studies should be due to the difference in adhesion of the 15 batches (15 different rolls) and not to the measurement system.

A new MSA study using the new sample collection should be done to also validate the 90°peel test.

Final conclusions

Once the 90°peel test is validated, as recommended above, it could be used. However, since it doesn’t allow to save time in the specimen preparation and the test is slightly more complicated than the 180° peel test, it is suggested to keep the 180°.

The z-direction pull test has been successfully validated and could be used as a quality control inspection. Although, taking into account the practical considerations, it is suggested to keep the 180° peel test until a more automatized and simpler UTM setup might become available that fits better the purpose for mass production. For instance, a setup where the operators should only prepare the specimen and clean the grips. This would further speed up the process and final turnaround time of this measurement, which is one of the key factors we are looking for. If such a system is developed, this could be a very promising testing solution.

For a deeper investigation of the electrode coating, the peel test seems to give more valuable information.

For a quicker investigation, such as a ‘go/ no go check’, the z-direction pull test would be the recommended solution.

Further work

Following further work is suggested from this project:

- Repeat the MSA study to validate the 90° with the new sample collection.
- Repeat the MSA study to validate the z-direction pull test with the crossed sample collection, once again, this time achieving a homogeneous coating detachment between the A side of the coating and the foil, as it happened during the method development stage.
- Further discuss with UTM suppliers to develop a semi-automated z-direction pull test setup.
- Find a solution to save time when cleaning the grips after the z-direction pull test. Different types of tapes could be tried.
- It would be useful to define a lower limit for the z-direction pull test, under which the adhesion is not acceptable. This would lead to have a ‘go / no go’ test, that would speed up the testing procedure.
- Once the quicker test is developed, an investigation on process parameters that affect coating adhesion can be carried out (binder quantity, drying rate and the resulting binder migration etc.).
- It would be extremely useful to find a method to verify the adhesion at- line in the production environment. For instance, a quicker test that could be done by process operators as a ‘go / no go’ test. If it is a “no go”, then the sample could be sent to the quality control lab for a deeper inspection. This could also help to reduce the high inspection rate frequency, as is currently the case, and reduce the workload of the analytical lab team.

- A study on how much the sheets are not homogeneous could be carried out. A certain number of sheets from the same roll and in different zones of the sheet could be tested. This should be done for different production runs This would help in the choice of the sample collection for further MSA studies.

List of abreviations

Al – Aluminium
AM – Active Material
Avg – Average
CMC – Carboxymethyl cellulose
Cu – Copper
DEC – diethyl carbonate
DMC – dimethyl carbonate
EMC – ethyl methyl carbonate
F – Failures
Fig. – Figure
Li – Lithium
Li+ – positively charged lithium ions
$LiCoO_2$ – Lithium cobalt oxide
LIBs – Lithium-ion batteries
LIB – Lithium-ion battery
Li-NMC – Lithium - Nickel Cobalt Manganese
$LiPF_6$ – Lithium hexafluorophosphate
NMC – Nickel Cobalt Manganese
NMP – N-methyl pyrrolidone
Op. – Operator
P – Pressure
Param. – Parameter/s
PVDF – Polyvinylidene fluoride
SBR – Styrene-butadiene rubber
Sdev – Standard deviation
T – Temperature
UTM – Universal Testing Machine
vs – versus

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