Master thesis in Nanotechnologies for ICTs

POLITECNICO DI TORINO

CHARACTERIZATION OF ION EXCHANGE MEMBRANES FOR ENERGY HARVESTING AND STORAGE DEVICES

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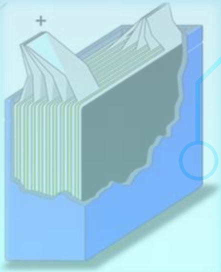
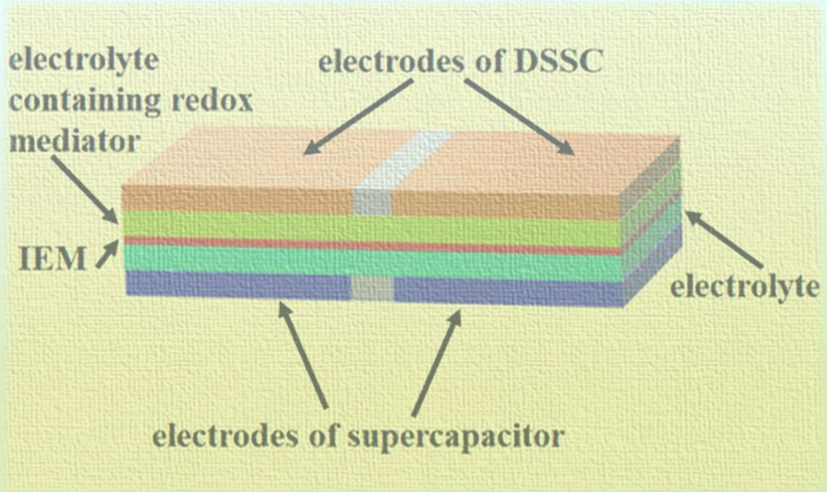
THESIS PURPOSE: CHARACTERIZING AN IEM MEMBRANE



From Tosukada,2008, ISBN 4526-047139

Contestualization: ***Realization of an integrated energy*** *Harvesting and Storage (**HS**) **device**. Integration of a Dye Sensitized Solar Cell and a supercapacitor, both with aqueous electrolyte, was intended.*

An Ion Exchange Membrane can be used to avoid "redox shuttling" (discharge of a supercapacitor due to Faradaic reactions).



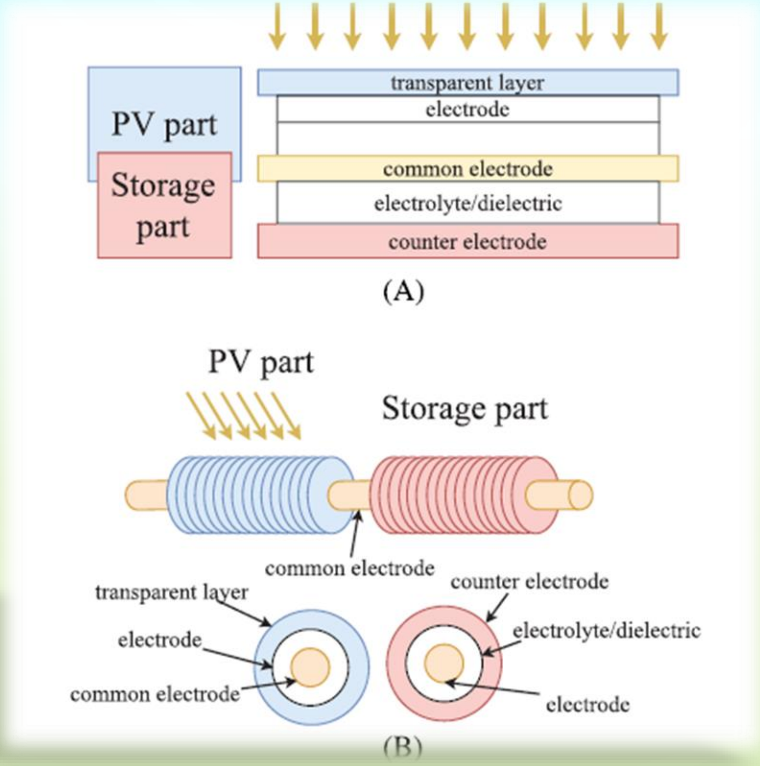
Goal: **characterizing an Ion Exchange Membrane (Nafion 117) to be used in an integrated HS device.**

INTEGRATED HS DEVICES

Devices which integrate the harvest and storage of energy.

Advantages:

- ❖ Compact devices;
- ❖ Solution for off-grid uses;
- ❖ Reduced ohmic leakages;
- ❖ Integrable in sensors;
- ❖ Green solution.



Planar vs. fiber-shaped, from [1]

DSSC:

- **Low cost;**
- **Good indoor efficiency;**
- **Eco-friendly;**
- **Flexible design;**
- Efficiency lower than other technologies.

+

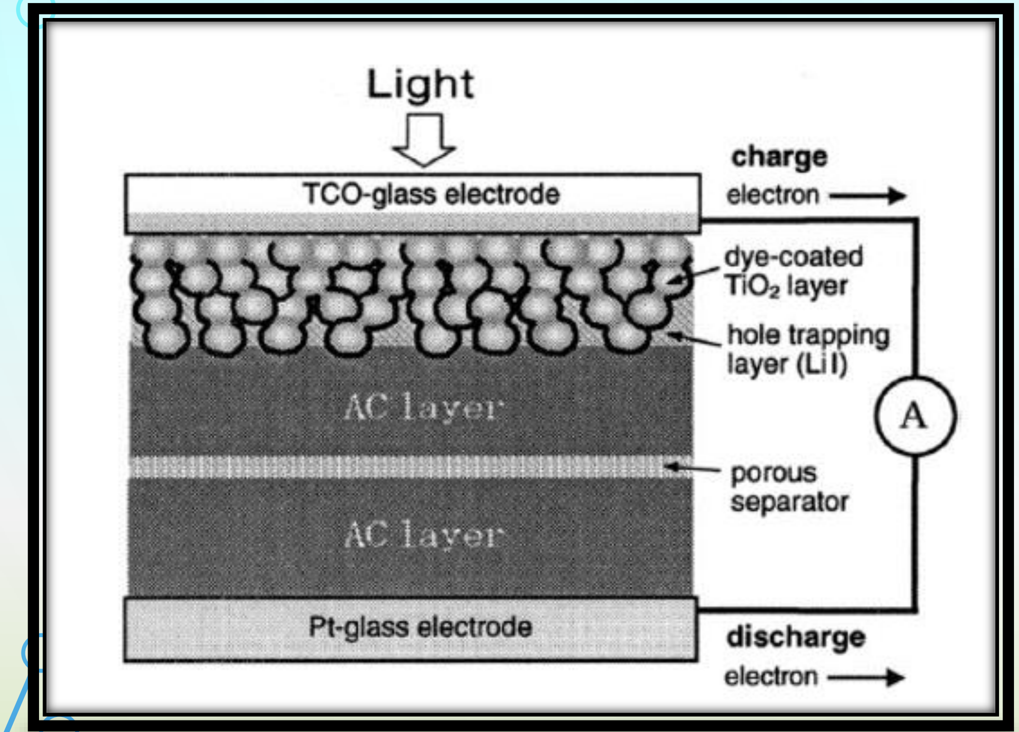
SUPERCAPACITOR:

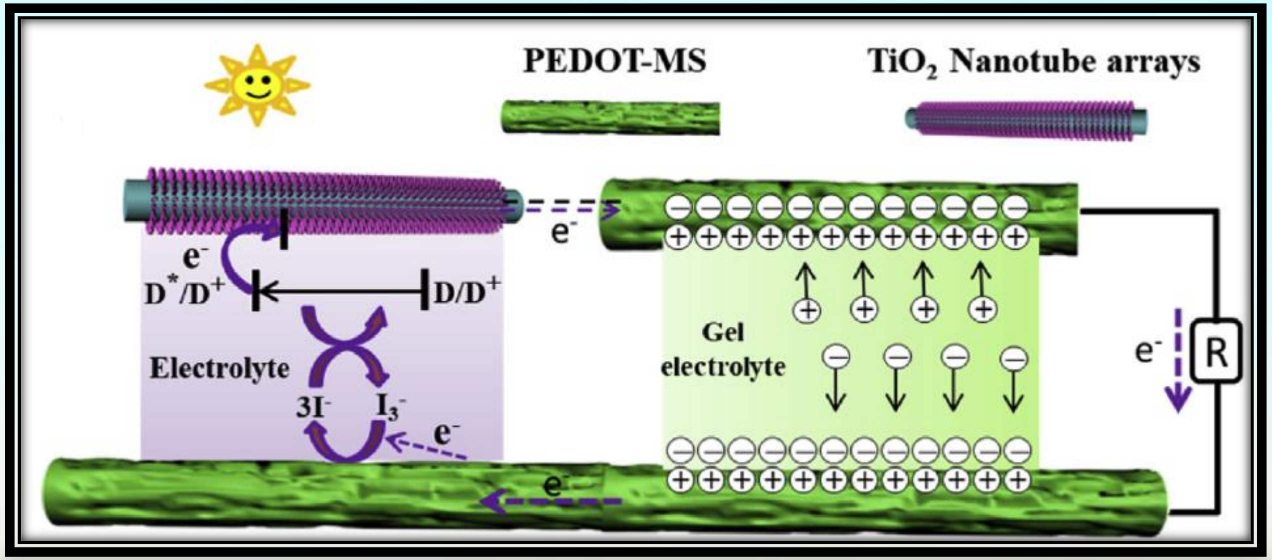
- **High power rates;**
- **Fast charge-discharge;**
- **Good stability for many cycles;**
- High self-discharge.

[1] V. Vega-Garita, L. Ramirez-Elizondo, N. Narayan, and P. Bauer. «Integrating a photovoltaic storage system in one device: A critical review». In: Progression Photovoltaics Research and Applications Vol. 27 (2019), pp. 346–370. doi:10.1002/pip.3093

2 INTEGRATED HS EXAMPLES

First photocapacitor: in 2004 by Miyasaka & Murakami, [2]

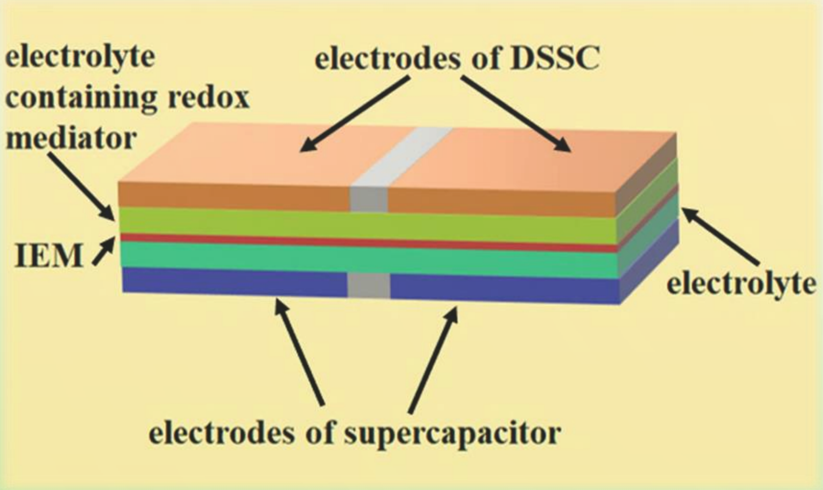




An example of fiber-shaped configuration: Wang & Co. in 2020, [3]

[2] T. Miyasaka and T. N. Murakami. «The photocapacitor: An efficient self-charging capacitor for direct storage of solar energy». In: Applied Physics Letters Vol. 85 (2004), pp. 3932–3934. doi:10.1063/1.1810630
[3] Z. Wang, J. Cheng, H. Huang, and B. Wang. «Flexible self-powered fiber-shaped photocapacitors with ultralong cycle life and total energy efficiency of 5.1%». In: Energy Storage Materials Vol. 24 (2020), pp. 255–264. doi:10.1016/j.ensm.2019.08.011.

CHARACTERIZATION OF THE MEMBRANE

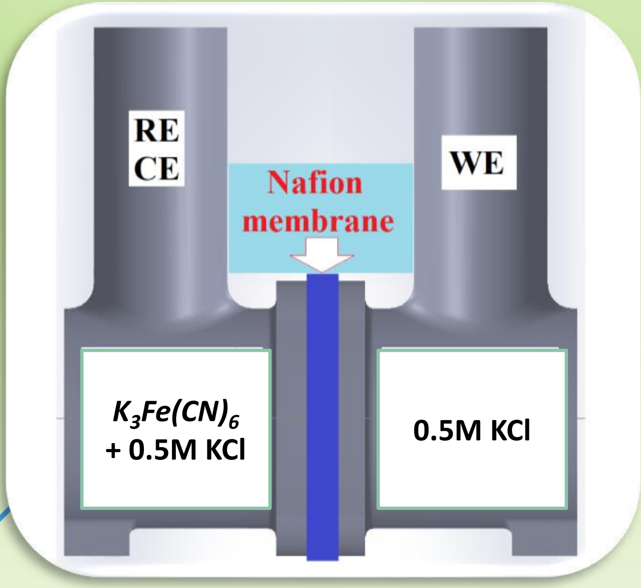


Characterizations:

1. ***Permselectivity;***
2. ***Passage of redox mediator.***

Redox mediator: $K_3Fe(CN)_6$

The passage of redox mediator was determined by measuring concentration variations in the chamber of working electrode.



Determination of diffusion coefficient with cyclic voltammetry, chronoamperometry and impedance spectroscopy.

Use of microelectrodes

Concentration determined by reversing relations with current or impedance.

MICROELECTRODES

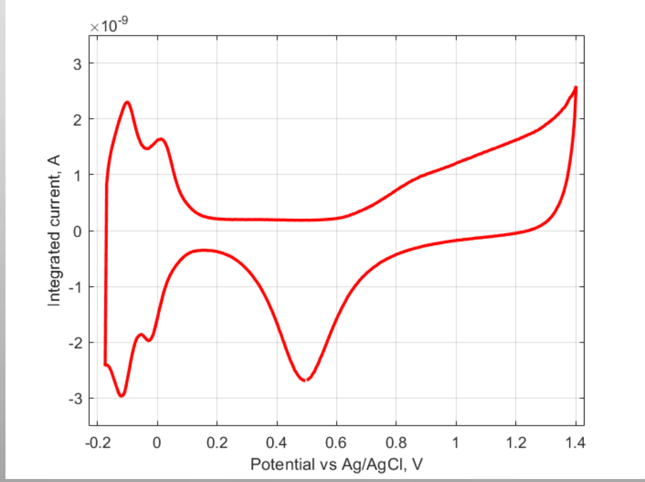
+ High sensitivity
+ Hemispherical diffusion region
+ Short times to reach steady state

- Currents in the order of nA
- Need for proper polishing procedures: Mechanical + electrochemical

Pt wire sealed in glass

Circular electroactive surface area (microdiscs)

3 analyzed diameters:
10 µm
20 µm
50 µm

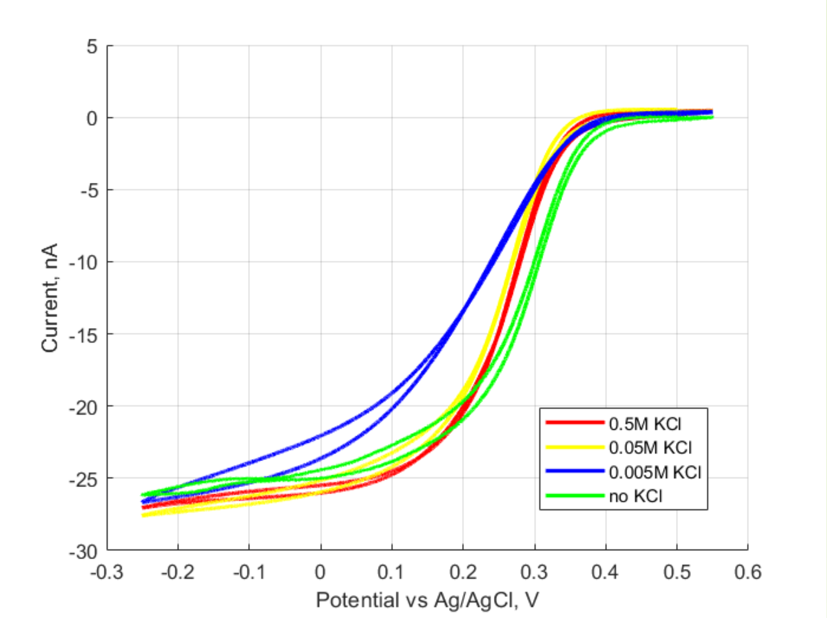


Evaluation of roughness factor and EDL currents

CV FOR DIFFUSION COEFFICIENT

KCl concentration	current	Diffusion coefficient
0.5M	26.93nA	$9.30 \cdot 10^{-6} cm^2/s$
0.05M	27.47nA	$9.45 \cdot 10^{-6} cm^2/s$
0.005M	26.46nA	$9.14 \cdot 10^{-6} cm^2/s$
0M	26.07nA	$9.01 \cdot 10^{-6} cm^2/s$

20 µm microelectrode with *different KCl conditions*



← Solutions with:
7.5mM $K_3Fe(CN)_6$;
xM KCl.

@ pH=3

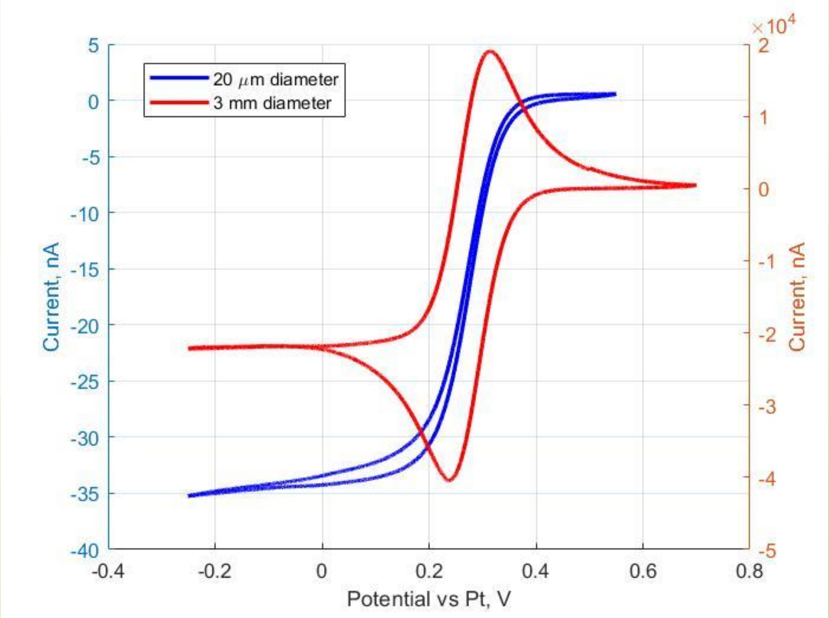
Evaluation of the reaction

$$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$$

Limiting current evaluation

$$i_L = 4nDFca$$

Comparing CV behaviour of a *microelectrode* with the one of a *macroelectrode*

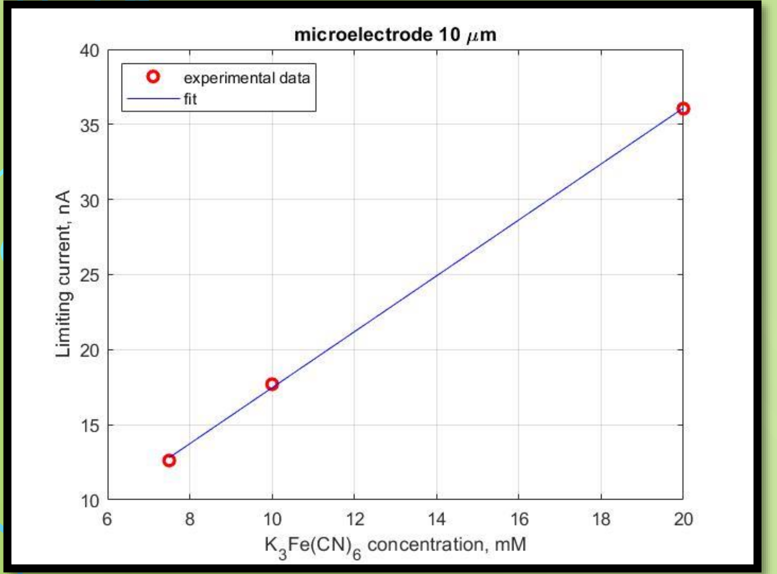


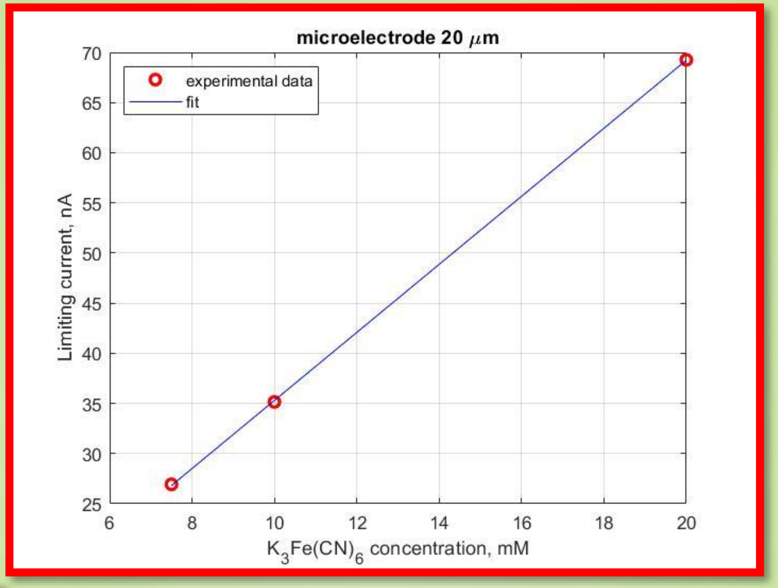
Scan rate: 5mV/s

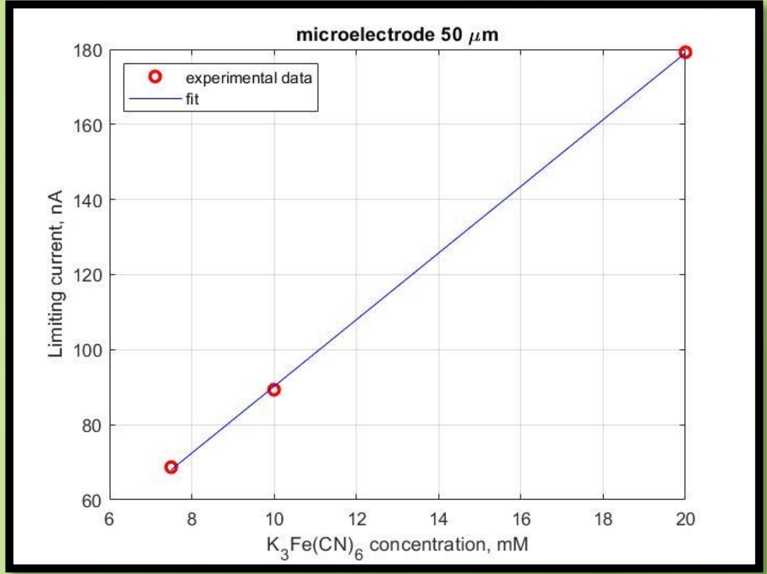
Nitrogen cover during measurements

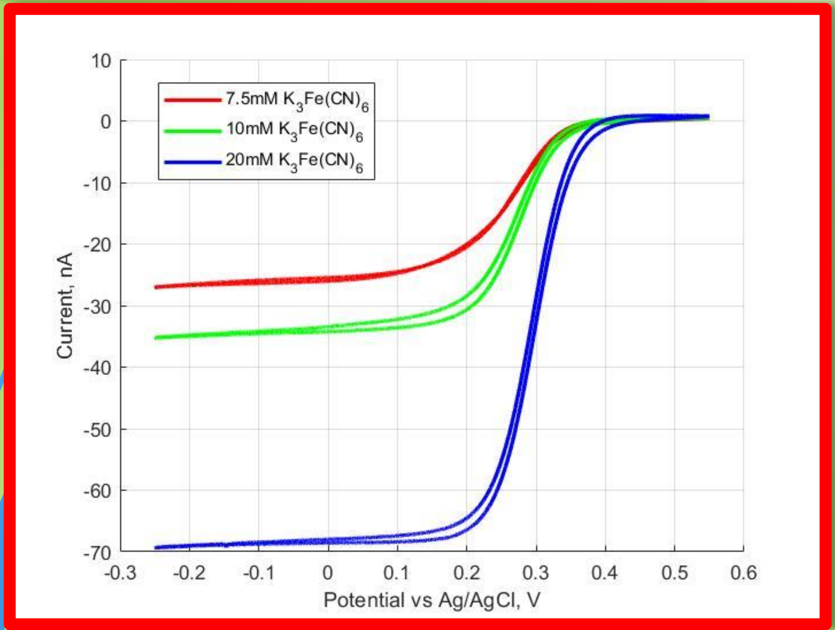
Experiments performed in a Faraday cage

CYCLIC VOLTAMMETRY CALIBRATION









Choice of 20 µm microelectrode:

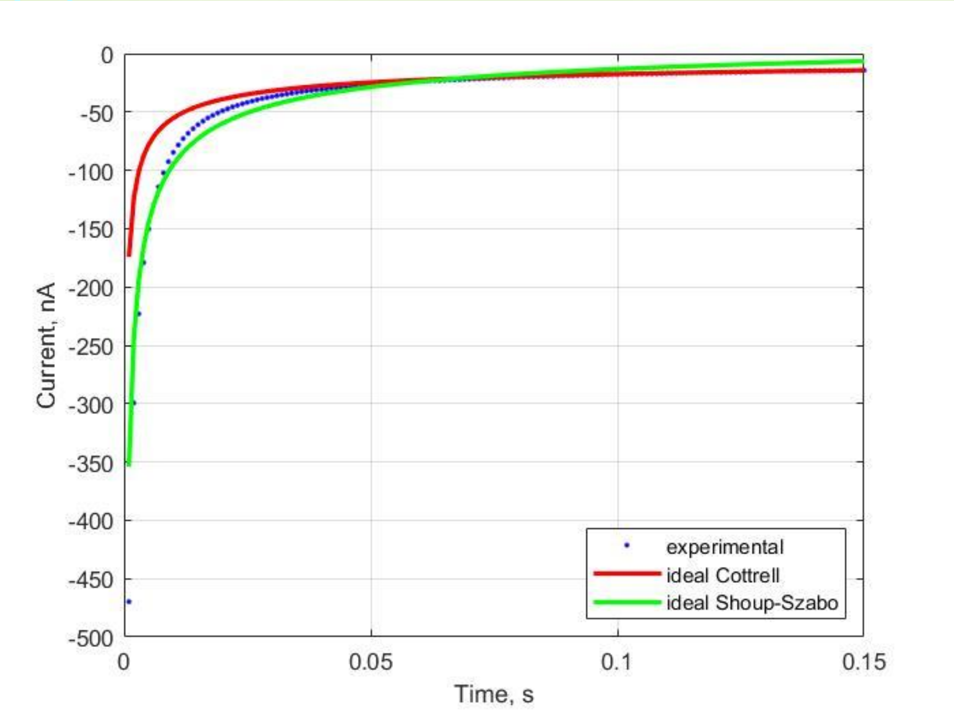
- ***Best concordance in different measurements;***
- ***Best surface geometry.***

20 µm microelectrode

current	concentration
26.93nA	7.5mM
35.15nA	10mM
69.26nA	20mM

$D = 9.13 \cdot 10^{-6} cm^2/s$

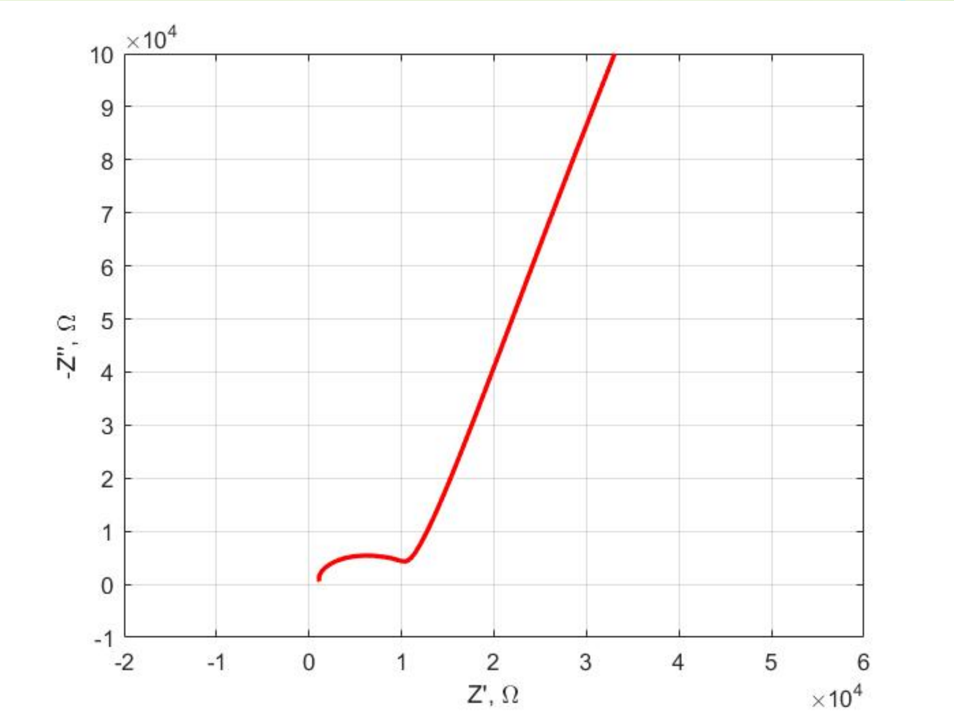
CHRONOAMPEROMETRY AND IMPEDANCE SPECTROSCOPY



Fast methods:
← Less than 1s
1-2 min →

Fit the current transient with Cottrell or Shoup-Szabo models.

Determine Warburg impedance.



Cottrell: $i = \left(\frac{8}{\pi^2}\right)\frac{nFAD^{1/2}c}{\pi^{1/2}t^{1/2}}$

Shoup-Szabo:

$i = 4nFDcr(0.7854 + 0.4431\tau^{-1/2} + 0.2146exp(-0.7823\tau^{-1/2}))$

where $\tau = \frac{Dt}{r^2}$

Warburg impedance: $Z_W = \frac{A_W}{\sqrt{\omega}} + \frac{A_W}{j\sqrt{\omega}}$

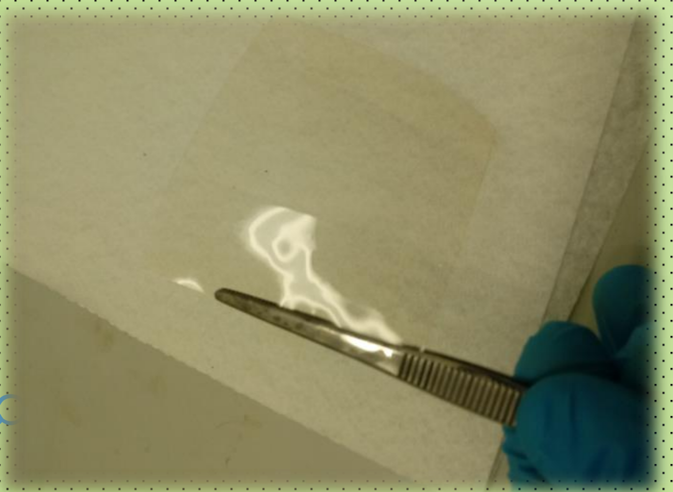
Warburg coefficient: $A_W = \frac{RT}{AF^2n^2c\sqrt{2D}}$

Worse agreement of results with respect to cyclic voltammetry

NAFION 117 MEMBRANE

Activation:

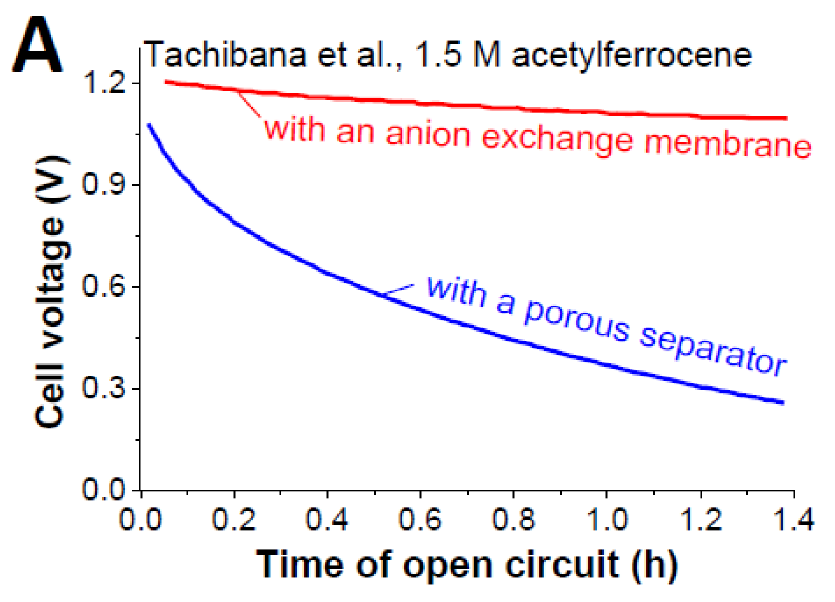
- Immersion in 3 wt% H_2O_2 for 1 h, at 80°C;
- Rinsing with deionized water;
- Immersion in 1M HCl for 1 h, at 80°C;
- Rinsing with deionized water;
- Immersion in 1M MCl for 1 h, at 80°C; (M = Li/Na/K)
- Rinsing with deionized water.



sulfonated tetrafluoroethylene-based fluoropolymer-copolymer

Cation exchange membrane: passage of cations is allowed, while anions are stopped

Ion exchange membranes are used in many fields, like redox flow batteries, electrodialysis and microbial fuel cells.
In this work important since avoids redox shuttling (*discharge of a supercapacitor due to Faradaic reactions*).



From [4] M. Tachibana, T. Ohishi, Y. Tsukada, A. Kitajima, H. Yamagishi, and M. Murakami. «*Supercapacitor using an electrolyte charge storage system*». In: *Electrochemistry* Vol. 79 (2011), pp. 882–886. doi: 10.5796/electrochemistry.79.882.

PERMSELECTIVITY

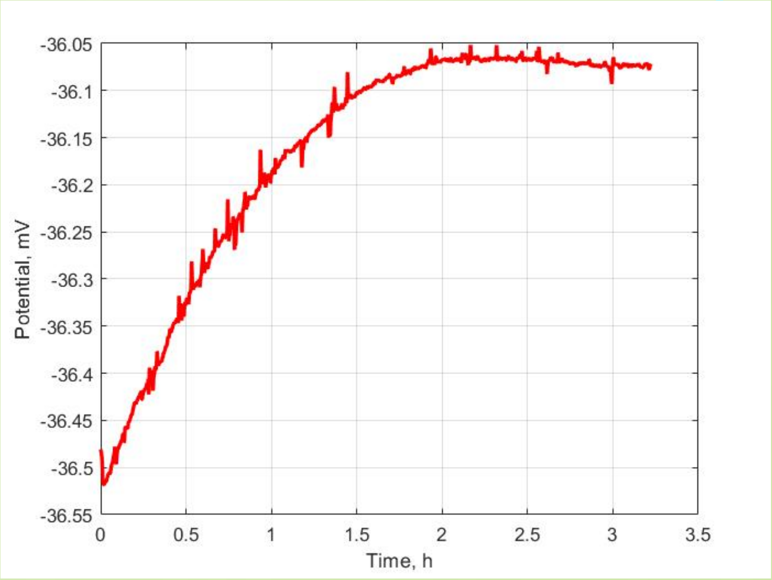
Quantification of the selectivity of the membrane to allow the passage of counter-ions, while blocking co-ions.

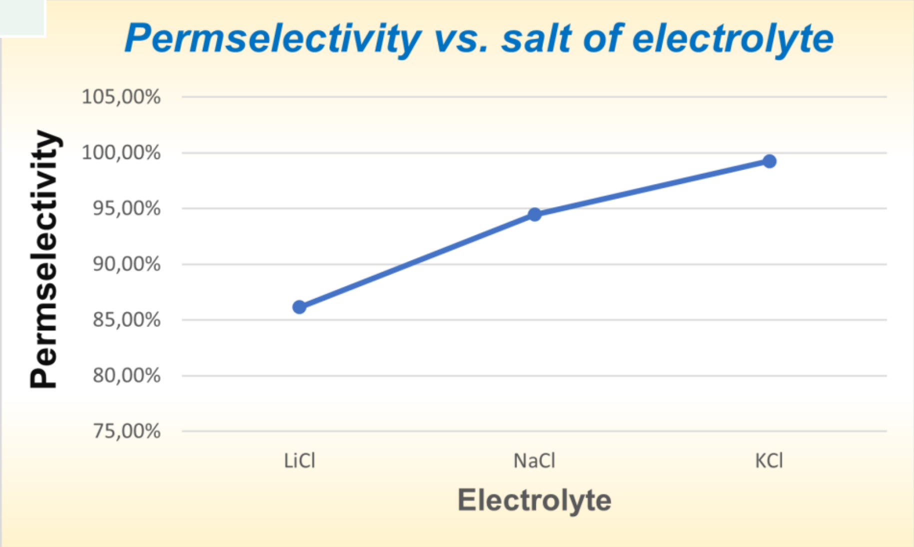
$$\alpha = \frac{\frac{E_{mem}}{E_{mem,ideal}} + 1 - 2t_g}{2t_c} \qquad t_g = \frac{|z_+|D_+}{|z_+|D_+ + |z_-|D_-}$$

solution \ activation	HCl	LiCl	NaCl	KCl
LiCl	77,11%	86,15%	82,49%	88,16%
NaCl	95,34%	94,45%	94,93%	100,15%
KCl	97,45%	99,24%	98,62%	98,77%

$$E_{mem,ideal} = -\frac{RT}{z_g F} \ln \frac{a_{0,5}}{a_{0,1}}$$

$$E_{mem} = E_{measured} - \Delta E_{ref} - \Delta E_j$$

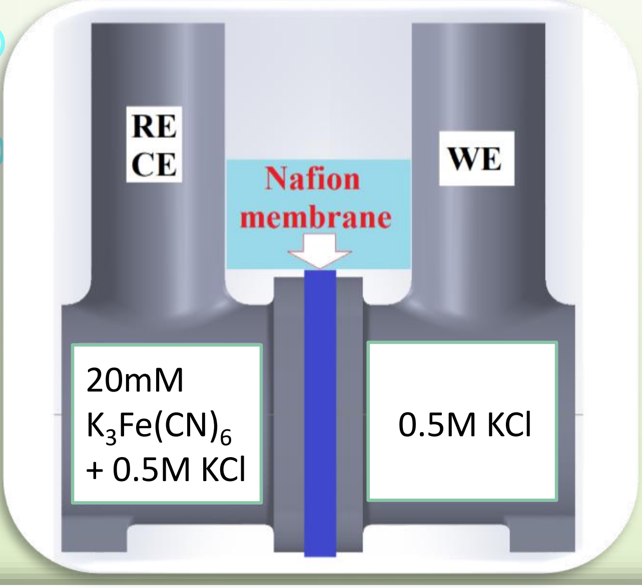




LiCl activation

Method and formulas from [5] R. S. Kingsbury, S. Flotron, S. Zhu, D. F. Call, and O. Coronell. «*Junction Potentials Bias Measurements of Ion Exchange Membrane Permselectivity*». In: *Environment Science Technology* Vol. 52 (2018), pp. 4929-4936. doi: 10.1021/acs.est.7b05317.

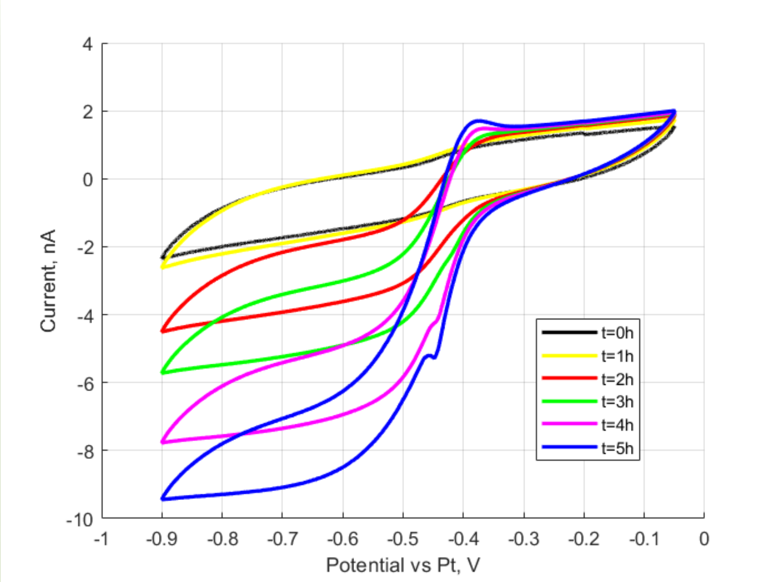
EVALUATION OF MEMBRANE PERFORMANCES

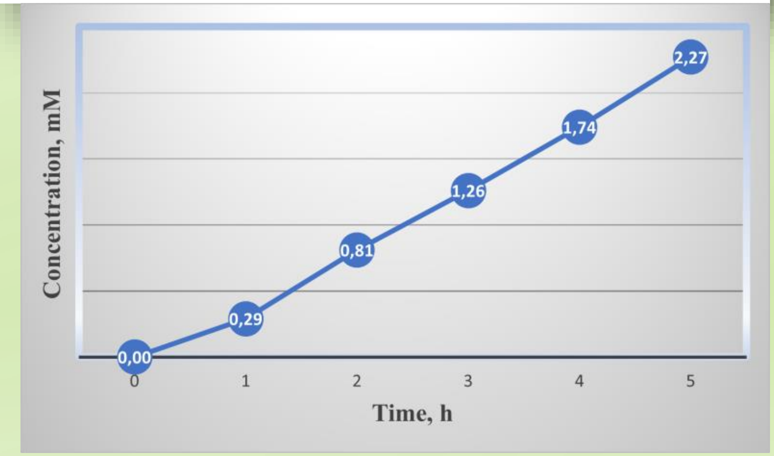


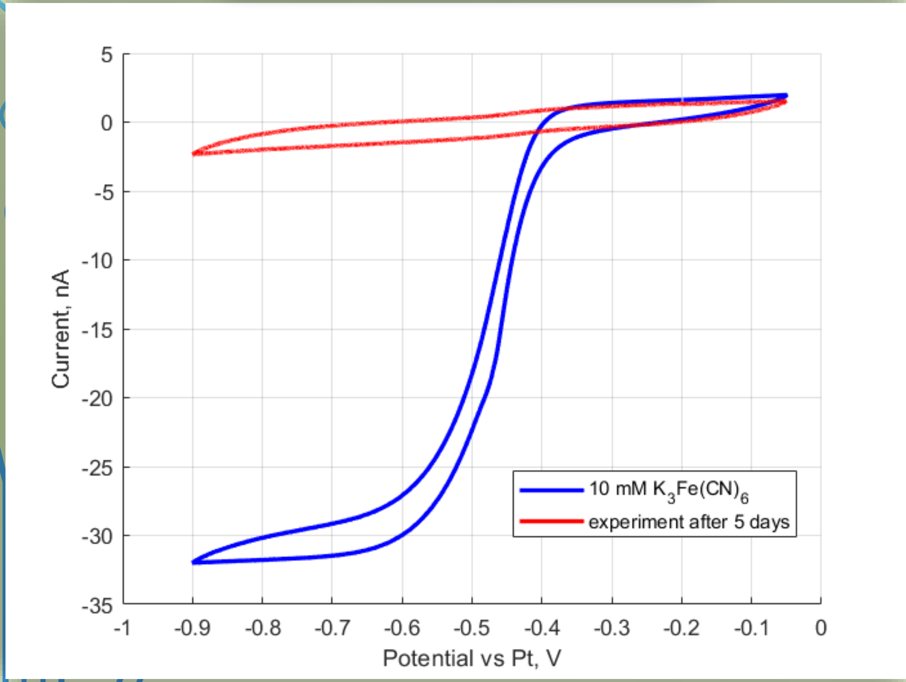
Counterproof: perforating the membrane with a 0.7mm needle

Reference and counter electrodes: **Pt rods**

Working electrode: **20µm microelectrode**







Results after 5 days of measurements

TREATED TITANIUM ELECTRODE TO CHARACTERIZE IEM

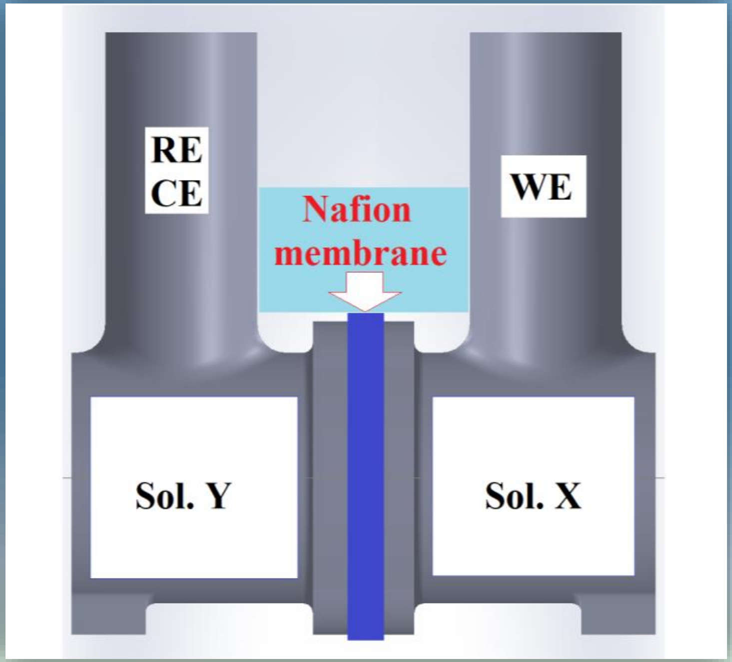
Slurry:

- 0.1mL of ethanol;
- 0.1mL of isopropanol;
- 30μL of Nafion® solution (5wt.%);
- 5mg of active materials (of which 85% Kuraray active carbons YP-50F and 15% carbon black TIMICAL SUPER C45).

Dropcasting on a Ti foil

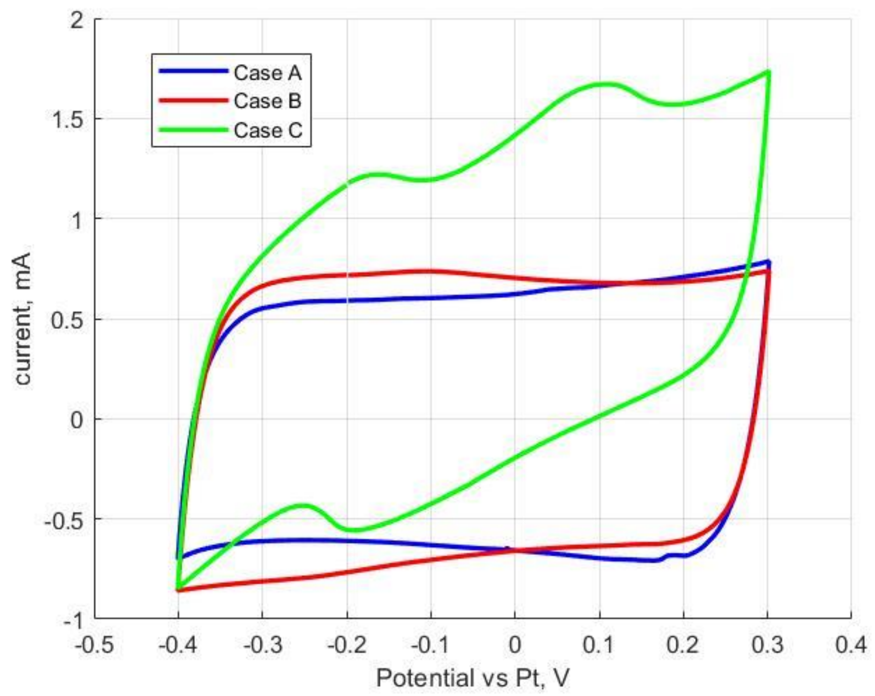
1.017mg of active material deposited

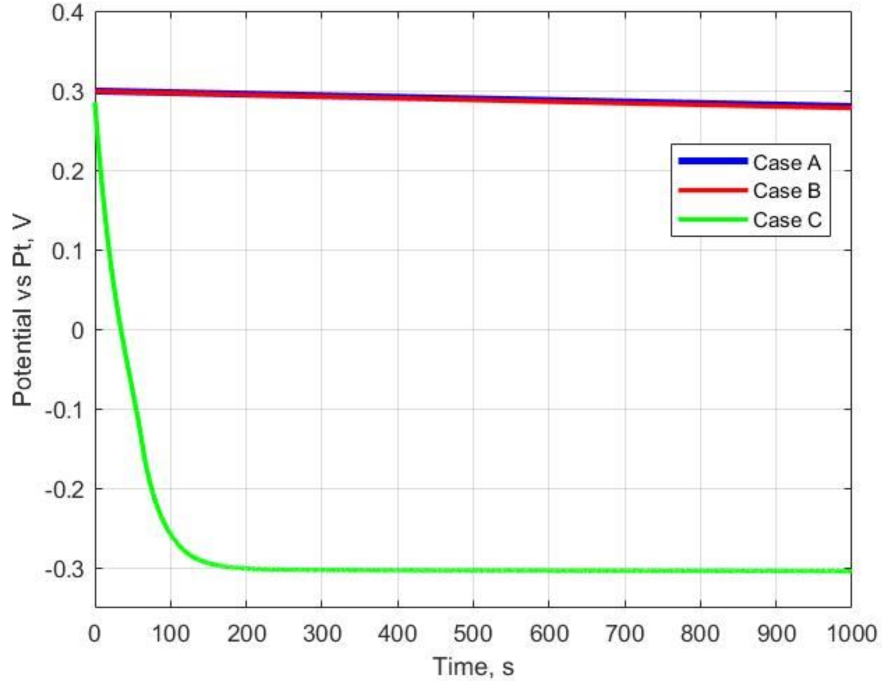
150mm^2 of active area



Three studied cases:

A) Sol. X = 0.5M KCl & Sol. Y = 0.5M KCl;
B) Sol. X = 0.5M KCl & Sol. Y = 0.5M KCl + 20mM $K_3Fe(CN)_6$;
C) Sol. X = 0.5M KCl + 0.5mM $K_3Fe(CN)_6$ & Sol. Y = 0.5M KCl + 20mM $K_3Fe(CN)_6$.





TREATED TITANIUM ELECTRODE RESULTS

- Capacitance: C = 29.7mF (normalized 29.2F/g)
- Coulombic efficiency: CE = 98.1%

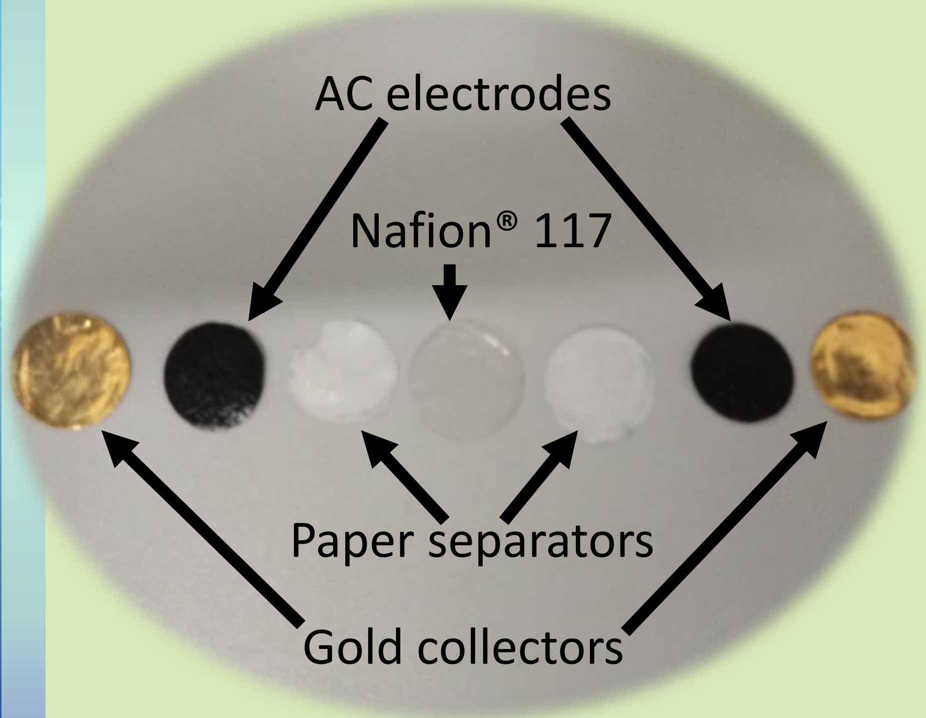
CV deformation in the system simulating a leakage (case C), due to presence of peaks (redox reaction).

Discharge in less than 3 minutes for case C.
Cases A and B held more than 96% of initial potential after 1000s.

Nafion membrane has stopped perfectly the redox mediator (results in agreement with only KCl).

Self-discharge is enormously increased when introducing redox mediator in the chamber of the supercapacitive electrode.

BUILDING A SUPERCAPACITOR



DISC-SHAPED ELECTRODES

Electrodes composition:

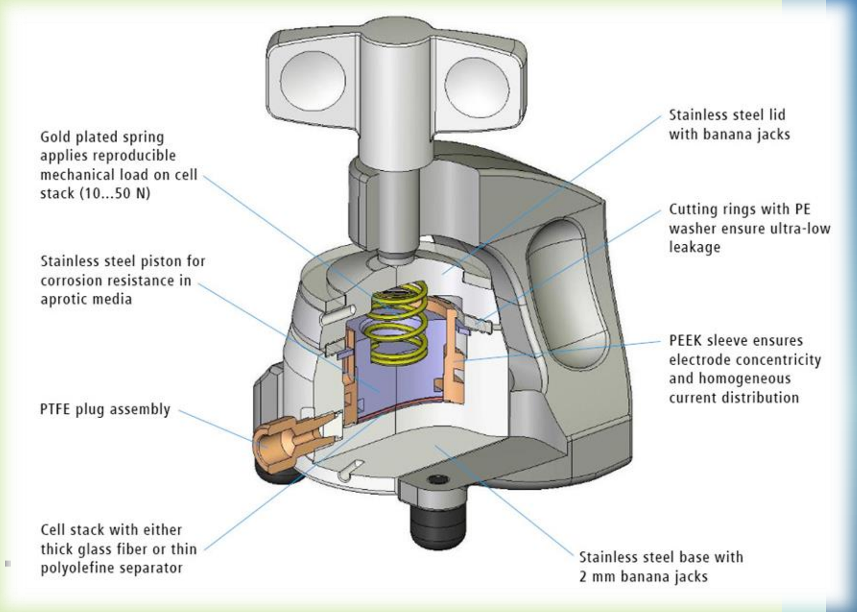
•**85% Kuraray active carbon, model YP-50F;**

•**10% TIMICAL SUPER C45;**

•**5% Polytetrafluoroethylene (PTFE).**

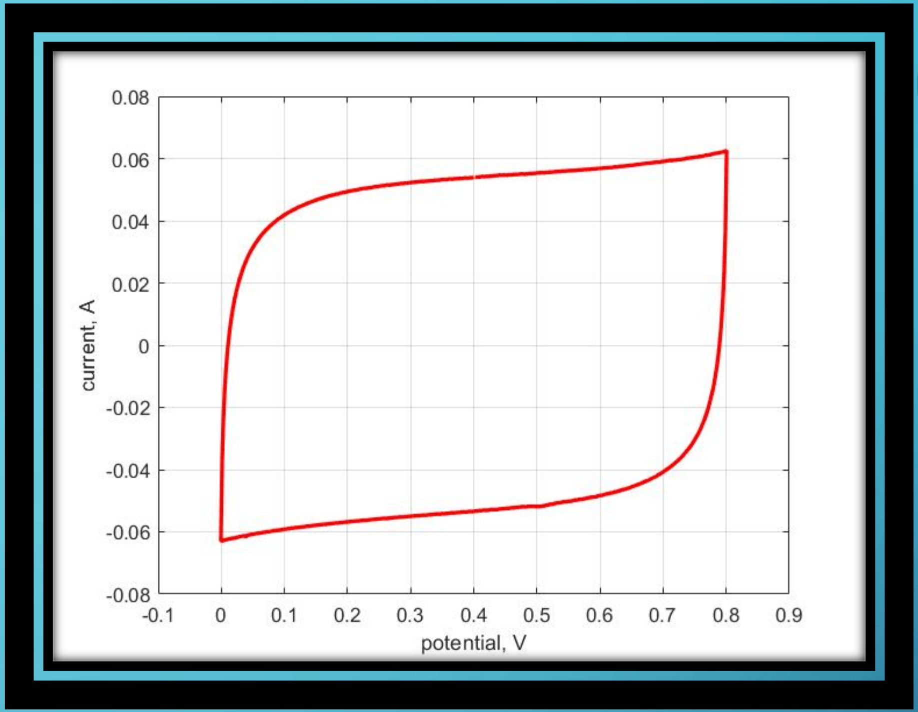
Using ethanol as solvent

Electrolyte: **0.5M KCl**

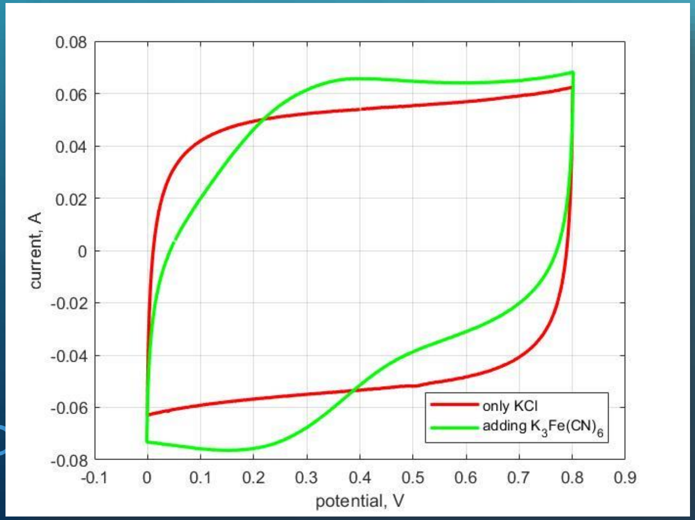


CV RESULTS

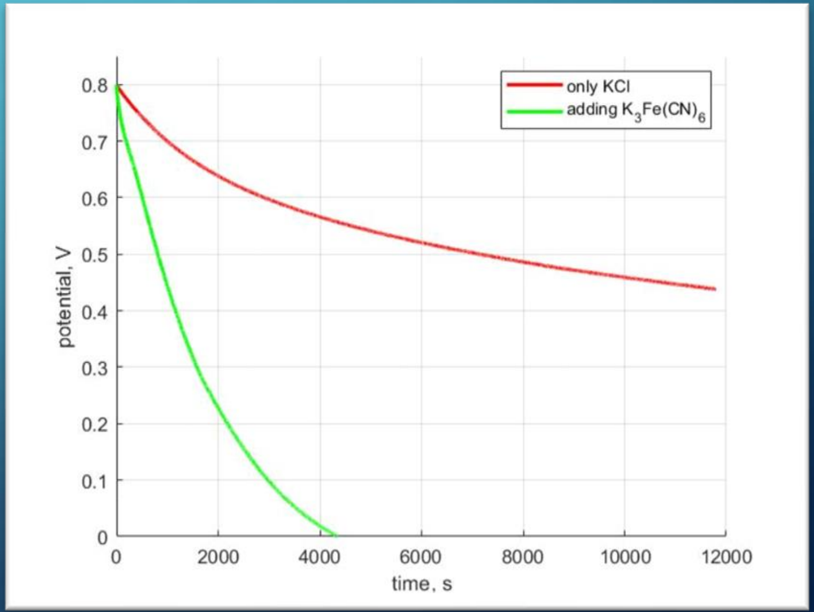
- Capacitance: 2,51 F
- Normalized capacitance per mass of active material: 37,48 F/g
- Operating window: 0 ÷ 0,8 V
- Coulombic efficiency: 99,1%
- Mass of electrodes: 35,0 mg and 35,5 mg



CV acquired at 20mV/s



Impact of redox mediator



CONCLUSIONS

- In this thesis work it has been found that a DSSC containing the redox mediator $K_3Fe(CN)_6$ (in acqueous solution with KCl supporting electrolyte) can be integrated with a supercapacitor which uses KCl as electrolyte.
- *A LiCl-activated Nafion 117 membrane can be a very good solution to prevent redox shuttling.*

FUTURE WORKS: integration of a DSSC with the considered electrolyte with a supercapacitor, where electrodes can be made as proposed. The studied membrane can be used in between.
The work will also continue with the substitution of $Fe(CN)_6^{3-}$ with I^-, using acenotrile al solvent, and maybe another Ion Exchange Membrane.

AKNOWLEDGMENTS:
Anna Aixala Perello, especially for the contribution to the part of permselectivity determination;
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