Aqueous Carbon Suspensions for Electrochemical Applications

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J3P : ENSIC NANCY 12 Juillet 2016

Recycling

Waste of Electrical and Electronic Equipment (WEEE)

Harvesting copper, tin and gold

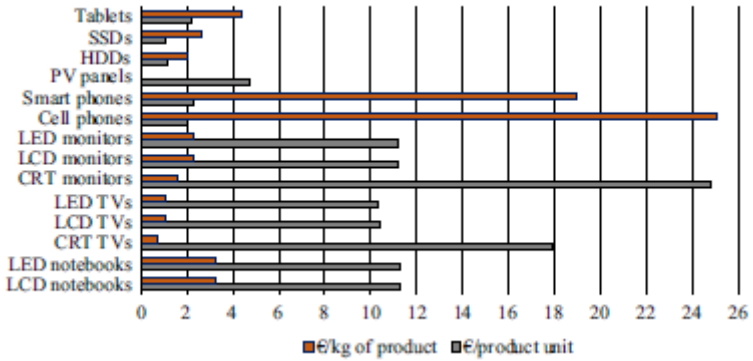


Table 5
Top-ten materials.

Materials	% Revenues
Gold	50.4
Copper	13.9
Palladium	9.5
Plastics	9.2
Silver	3.6
Aluminium	2.5
Tin	2.0
Barium	1.8
Platinum	1.7
Cobalt	1.6

81,1 % Total
et
89,9 % metals

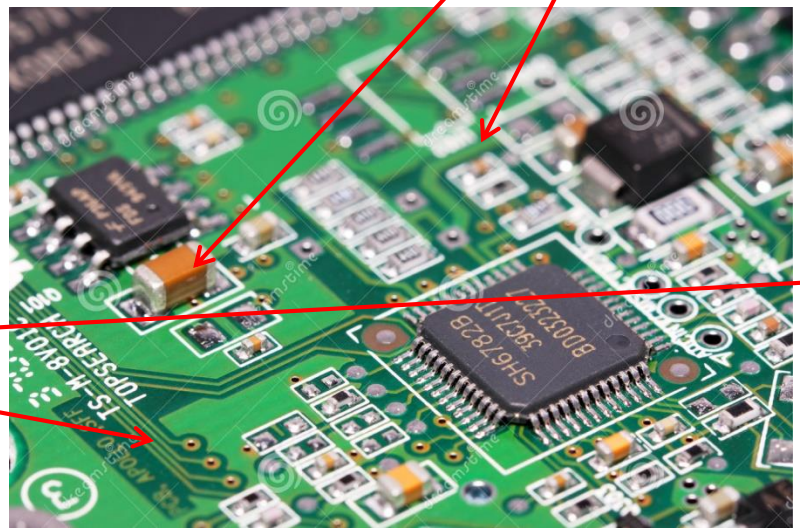
F. Cuchiella et al. RenewableandSustainableEnergyReviews51(2015)263–272

Choice of a model waste

microelectronics

Cu, Ag
Ta_2O_5

Model sample



interconnection
Au Cu
Sn Pb Ag

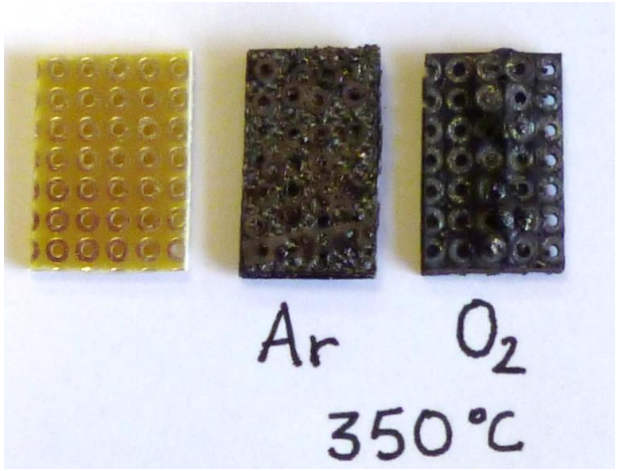
Conventional process pyrolysis at 900°C produces a lot of pollution

Alternative is high energy milling to separate metals froms plastics but better woks with pins and barbs

Mechanisms
Reproductibility

Electrolixiviation of electronic waste

ground

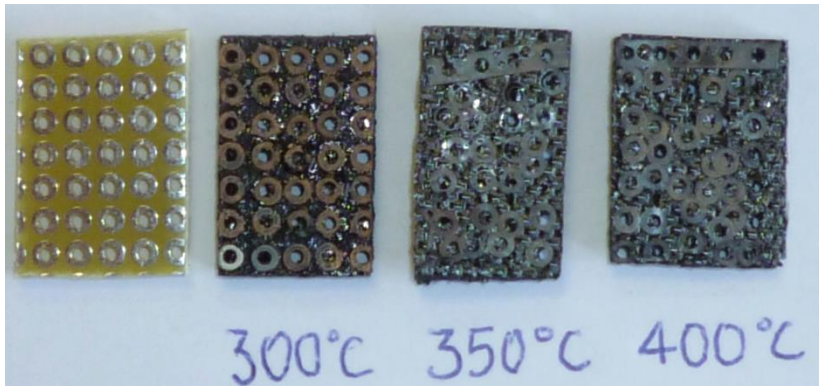


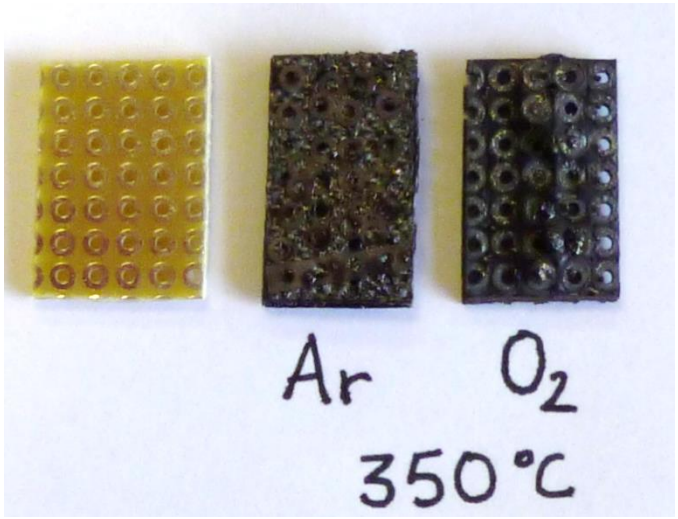
«Torrefied »

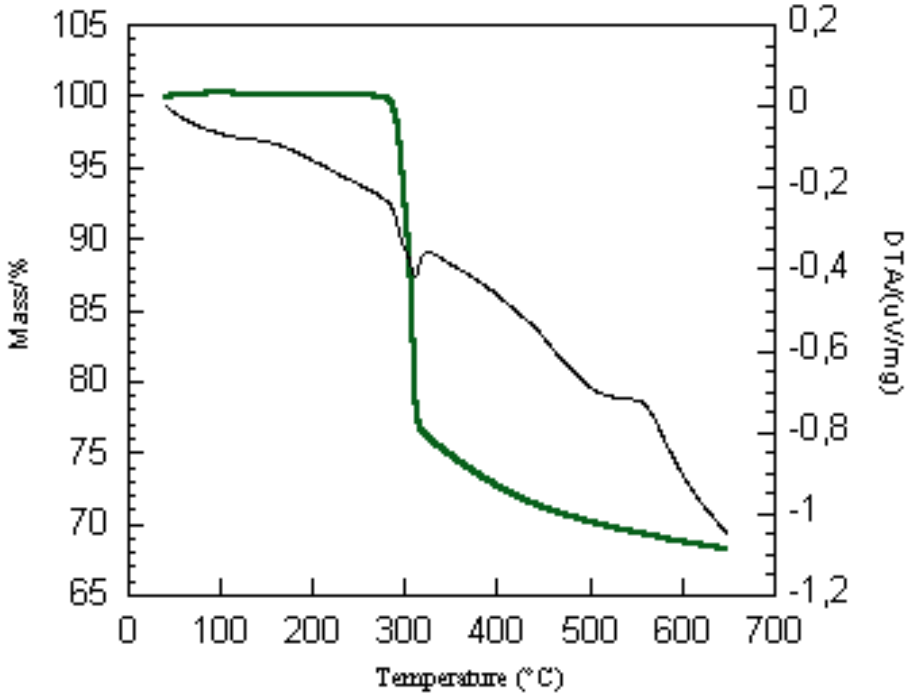
Removes protection

Extraction
Sn, Cu Ag Au

1) thermal decomposition

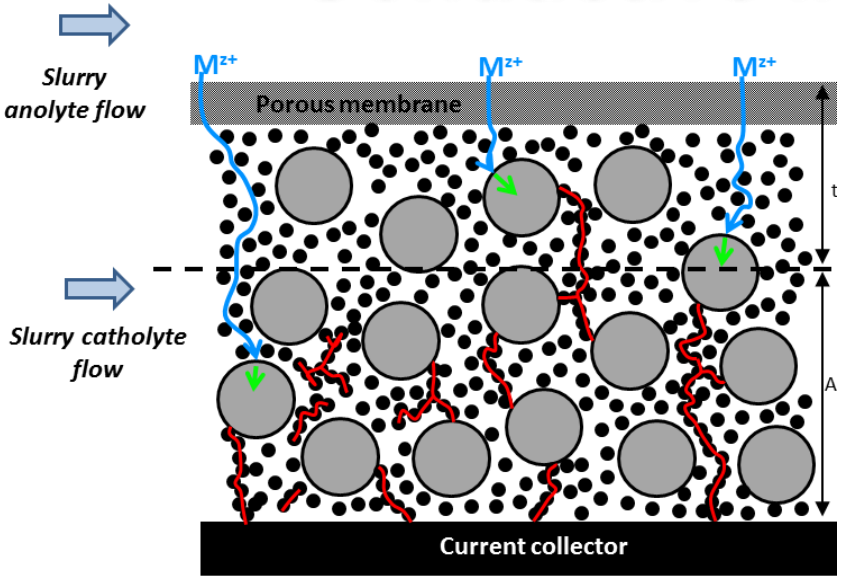






varnish decompose at 300°C
avoid oxidation Cu/CuO ➔
inert atmosphere

Conductive inks



Hydrogen Fuel Cells commonly are 1000 mW/cm^2

Hope for 100 mW/cm^2 (actual performance ≈ 40mW/cm^2)

Potentiel : 2 V (water)

Current density : 50 mA/cm^2

1m^2 = 5 kW

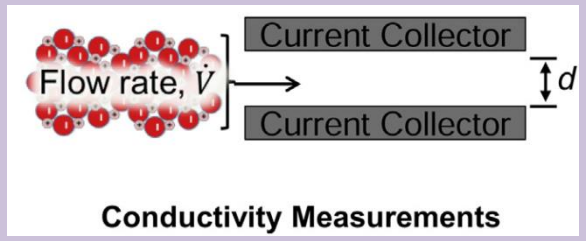
Assume 20% Voltage drop ohmic 0.4 V

Resistance should be less than 8 ohm /cm➔ s ≈ 60 mS/cm

Both ionic and electronic !

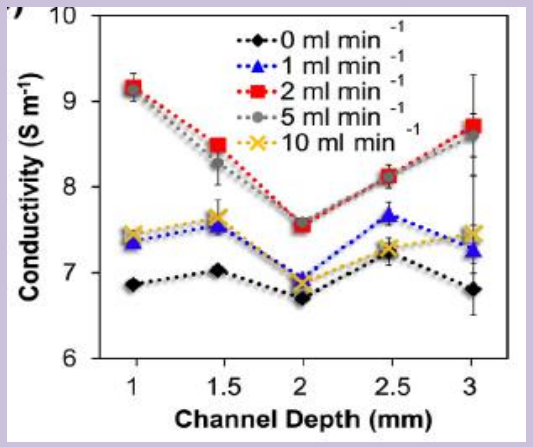
Aqueous solution ionic conductivity OK ➔ electronic ?

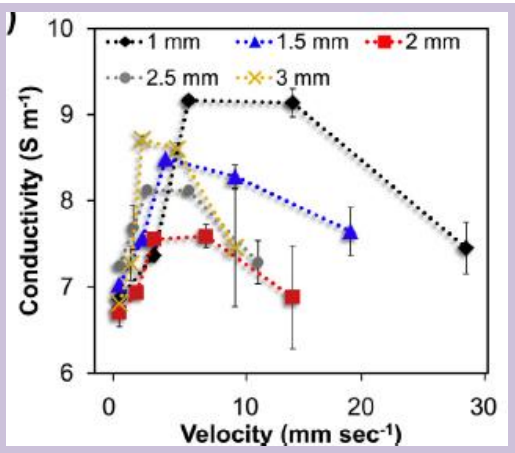
Conductivity in the literature

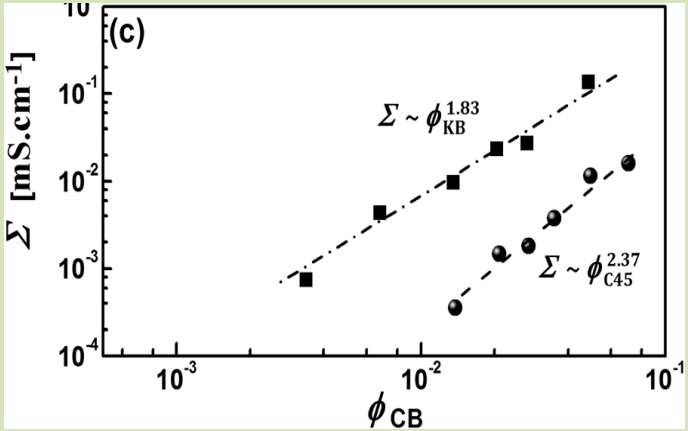


~90 mS/cm

Dennison et al. *J. Power Sources* **2014**

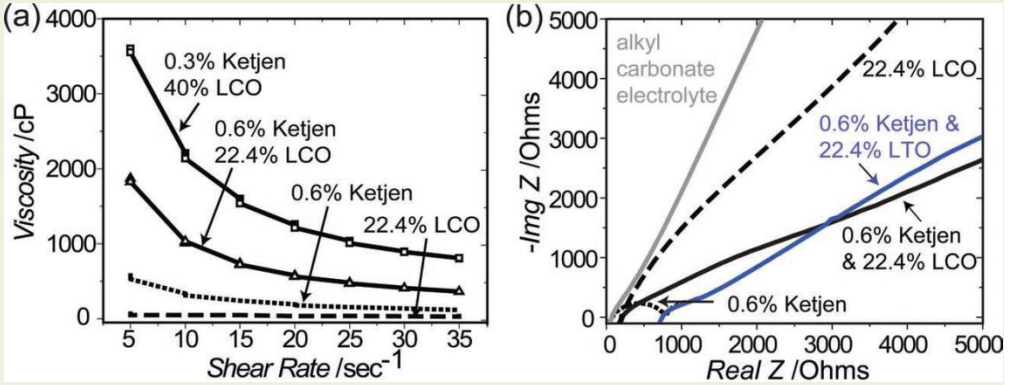






~1.10^{-1} mS/cm

Youssry, M. et al. *Phys. Chem. Chem. Phys.* **2013.**



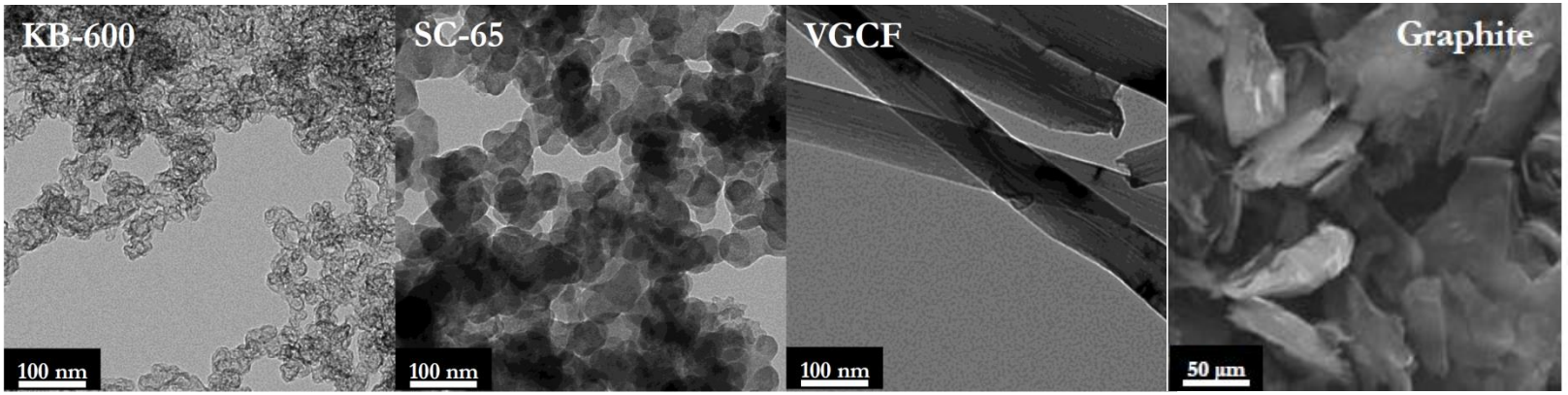
~6.10^{-2} mS/cm

Duduta, M. et al. *Adv. Energy Mater.* **2011.**

Controversy ?

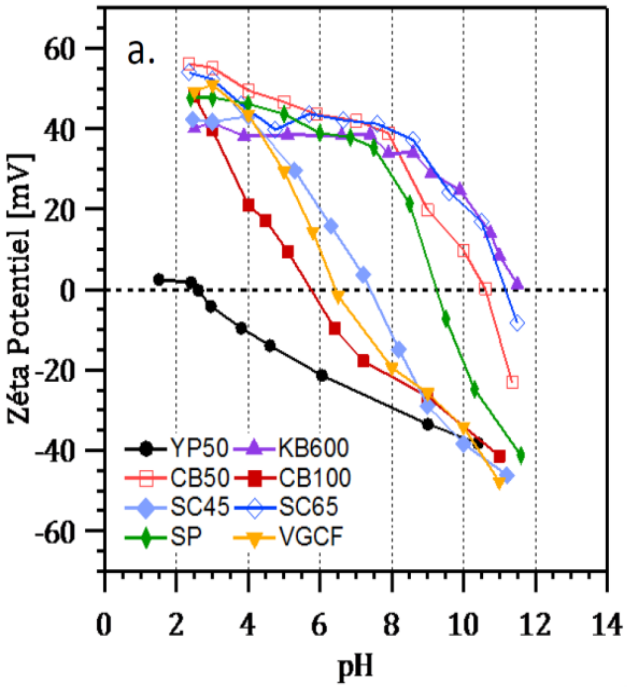
Carbons studied

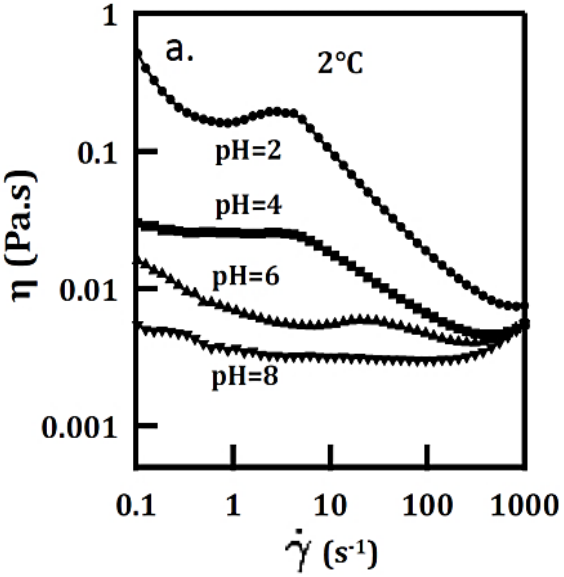
Carbones	Références	Source
Graphite	Graphite powder, <20 µm, synthetic	Sigma-Aldrich
CB100%	Carbon black, acetylene, 100% compressed	Alfa Aesar
SP	CARBON SUPER P	Timcal / Imerys
SC45	C-NERGY™ SUPER C45	Timcal / Imerys
SC65	C-NERGY™ SUPER C65	Timcal / Imerys
KB600	Ketjenblack EC-600JD	AkzoNobel
VGCF	Vapor Grown Carbon Fiber	Showa Denko
YP50	Carbon YP-50F coconut base	Kuraray

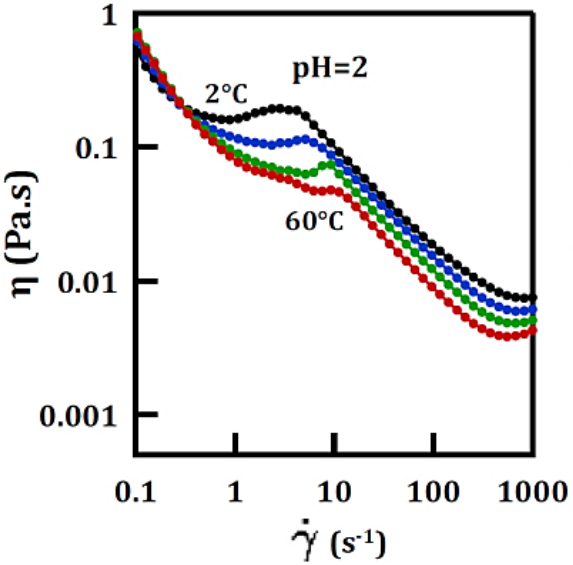


Rheology of suspensions YP50

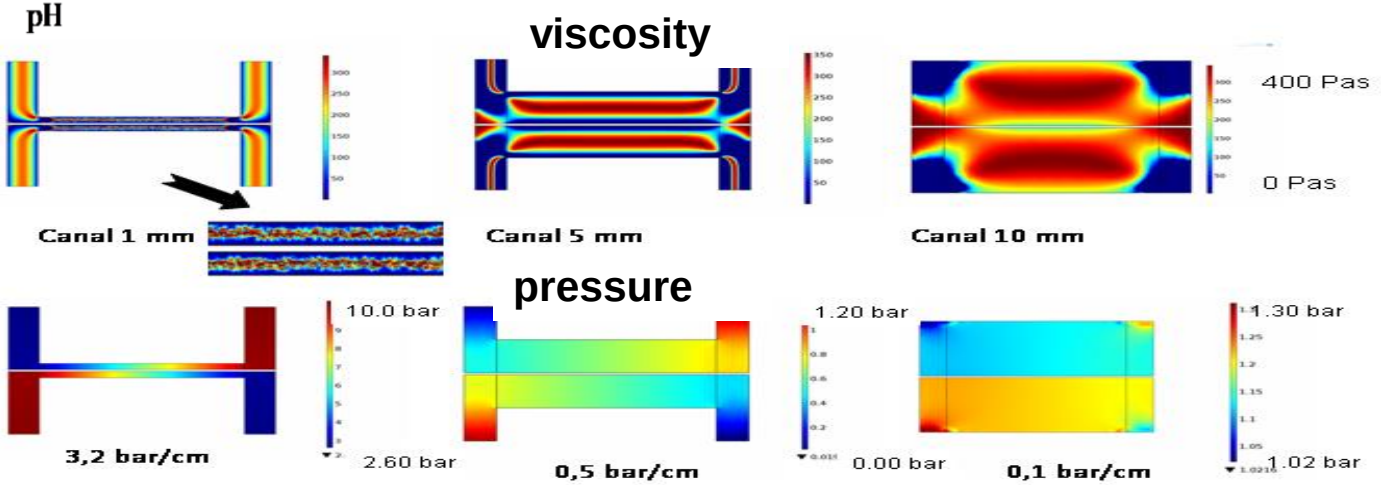
YP50
10% mass
water





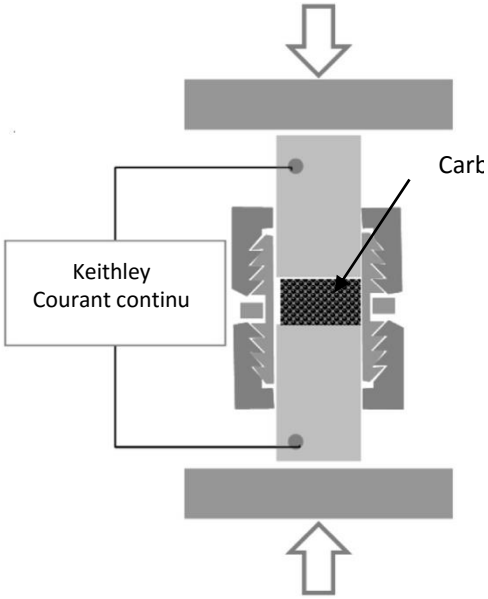


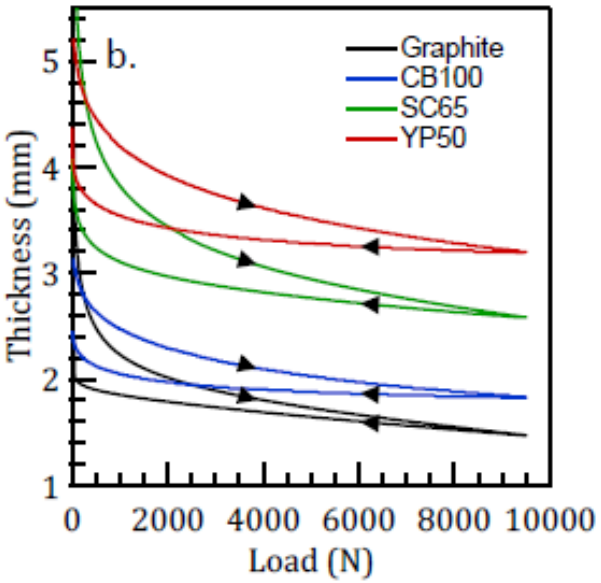
Channel 5 mm
Stay less
than 100 Pas
Pressure drop
< 1 bar/10 cm

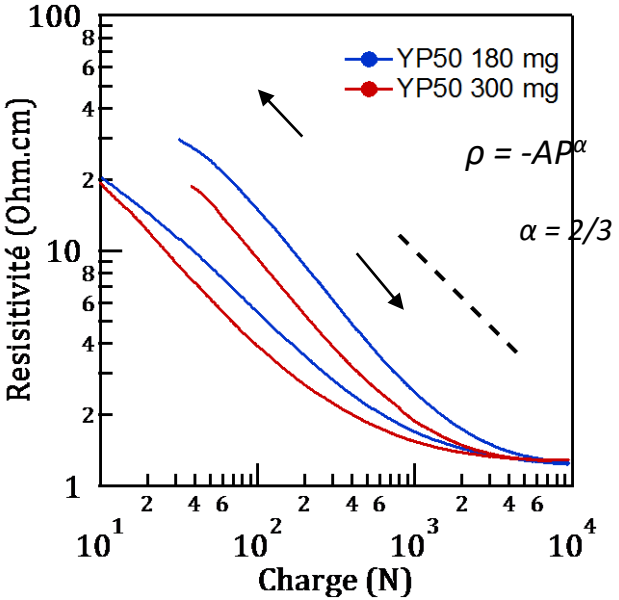


Simulation Comsol Kevin Croué (IRCP/Amiens)

Conductivity of powders







Carbons	Conductivity (9,5 kN)
Graphite	810 mS/cm
CB100%	550 mS/cm
SC65	669 mS/cm
YP50	800 mS/cm

Conductive carbon inks

1

% known mass of carbon
+water millipore + 1M Na_2SO_4 or 0.5 M $CuSO_4$

2

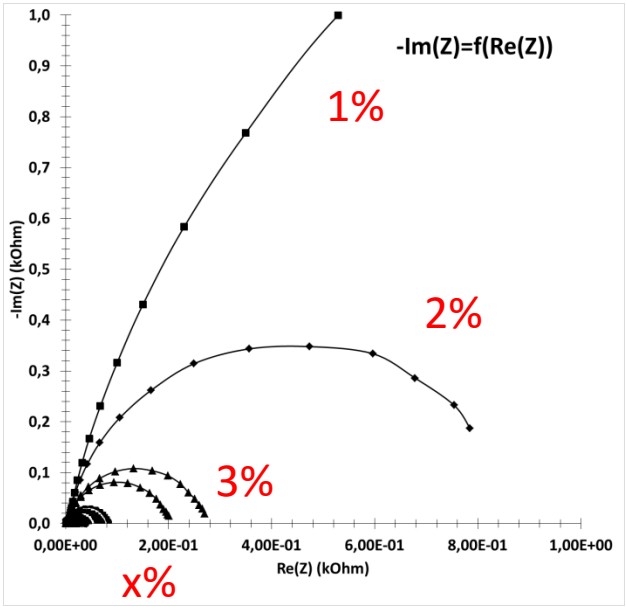
High shearing mixer (ultraturax)
+ 45 mn magnetic stirring

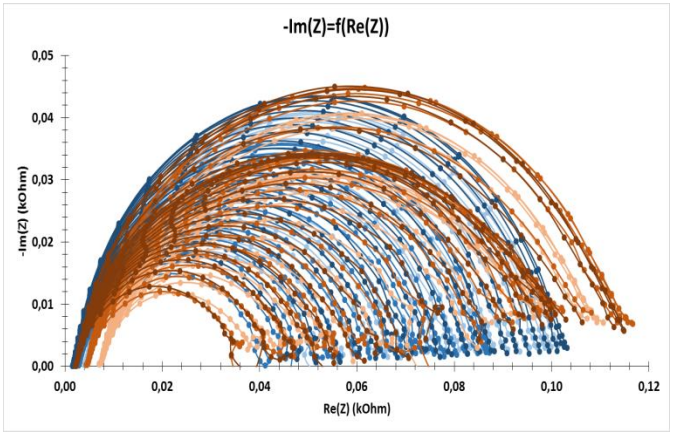
YP50(14%)/CB100(2%)
16%mass.

Carbon black CB

Conductivity versus concentration

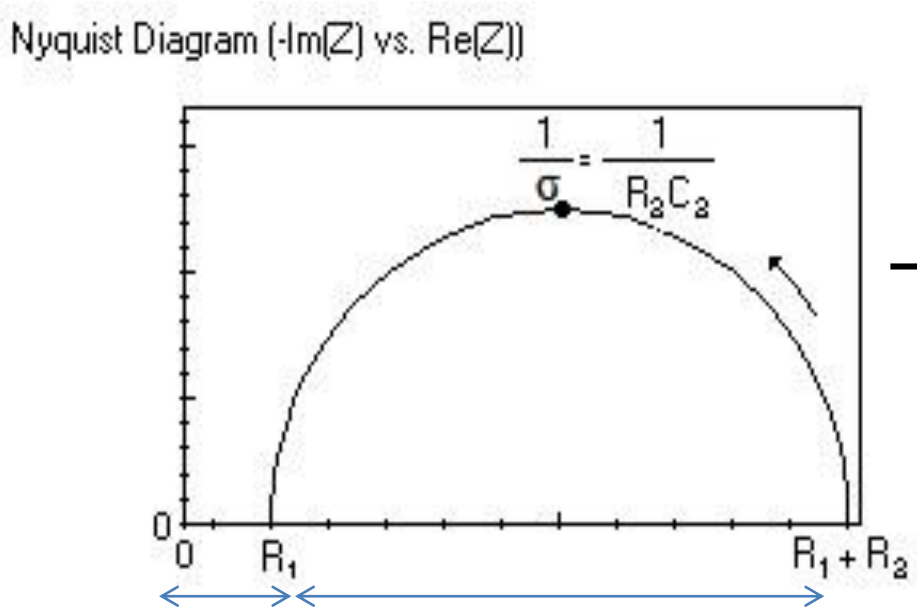
Only electrolyte is ejected





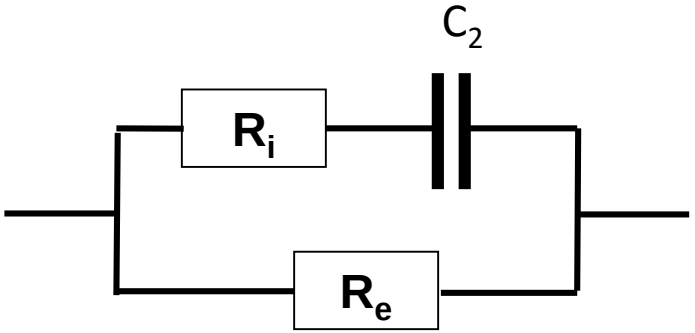
Different colors
=
different thickness

analysis



Both

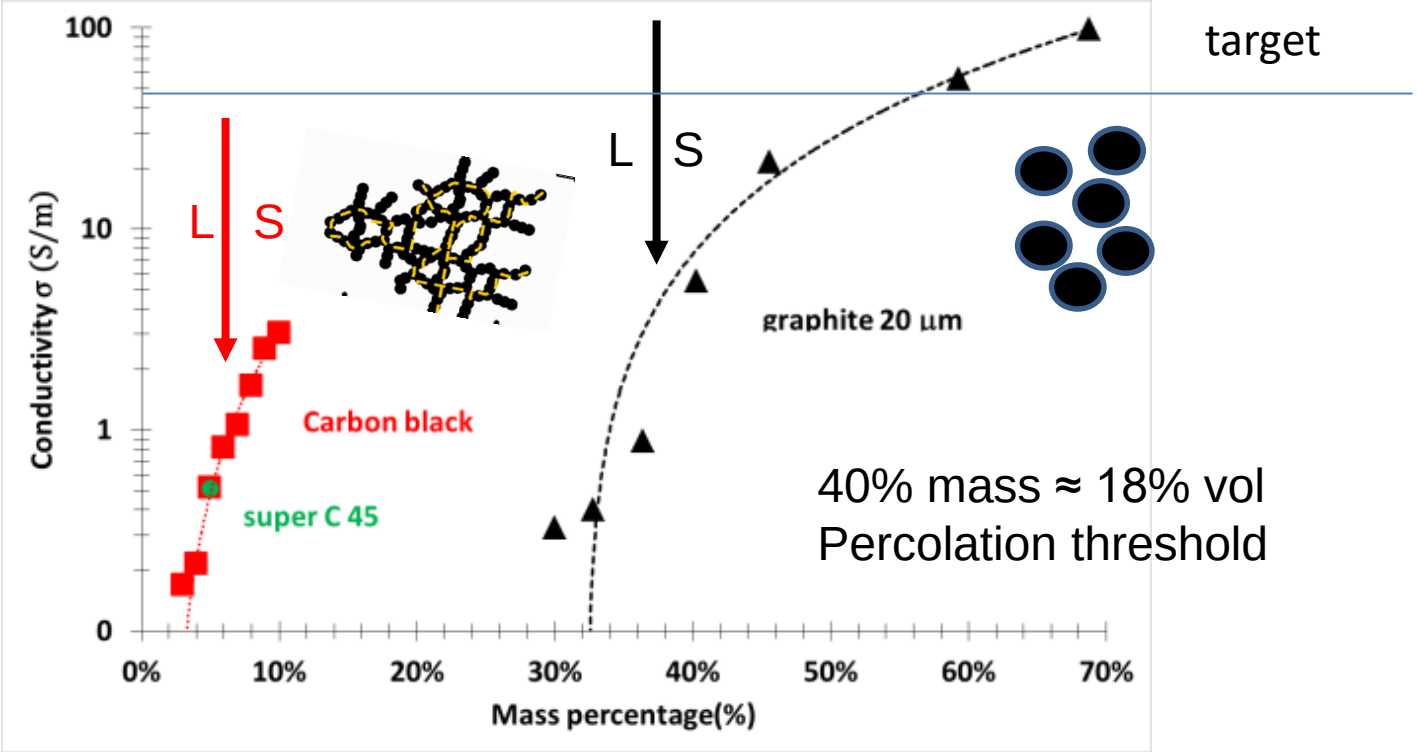
Electronic contribution



$R_2 = R_e$

$1/R_1 = 1/R_e + 1/R_i$

Conductivity Results



Graphite large particles allow higher loadings
Only graphite is near to target but 6 S/m = 60 mS/cm at 30% loading
Paste can be stirred 60 mS/cm (30%)
Inks give 3-5 ms/cm
But unstable suspension (sedimentation)

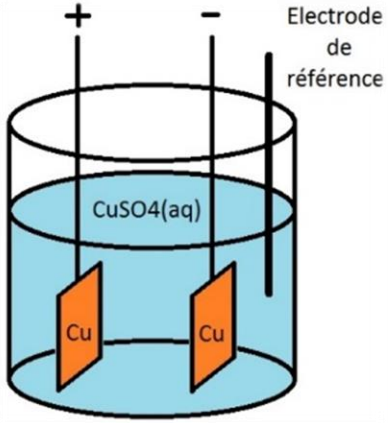
Needs constant stirring or chermical additives (plasticizers)

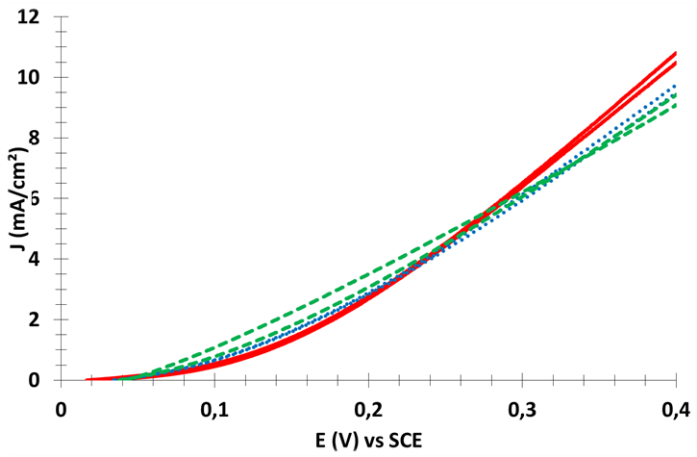
Electrolixiviation of Cu,Sn

Graphite slurry
needs constant steering

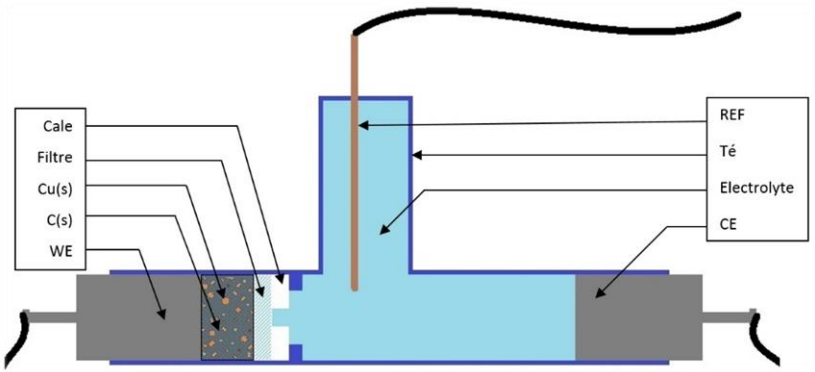
electrochemical copper extraction

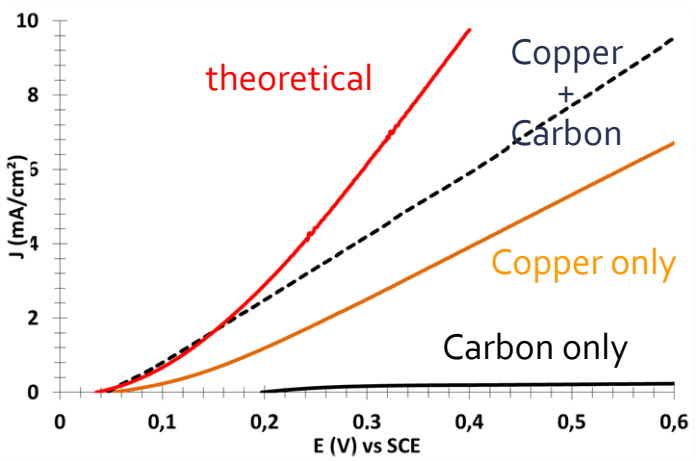
Copper surface current





Copper powder

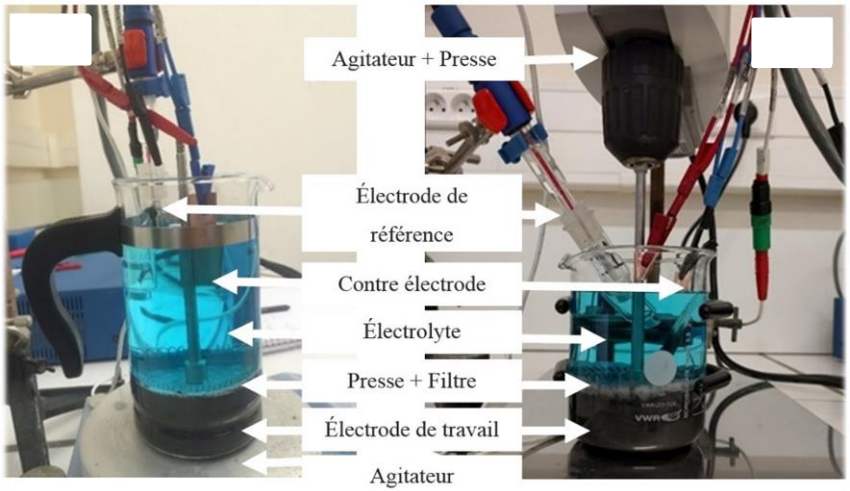




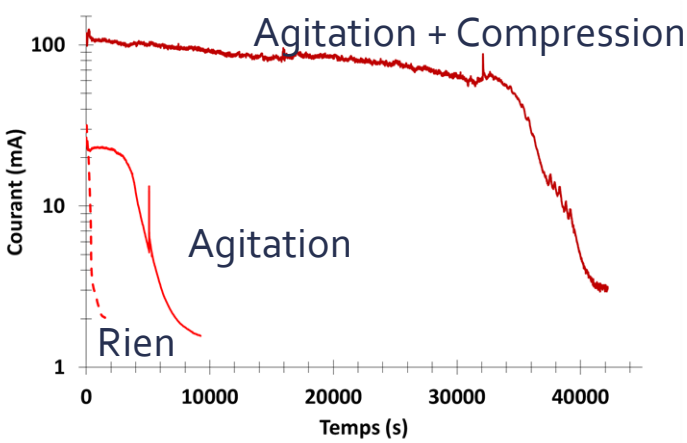
Carbon : improves the electronic contact with the powder

RÉCUPÉRATION DU CUIVRE

- **La cellule Filtre-Presse**



- **Électrolyse :** Cuivre + Carbone



- $\eta_{récupération} = \frac{m(métal)*n*F*0{,}28}{M(métal)} = \mathbf{90\%}$
- $\eta_{faradique} = \frac{Q_{expérimentale}}{Q_{théorique}} = \mathbf{95\%}$

- **Encre :** amélioration du contact électrique
- **Agitation :** Maintien du courant
- **Compression :** Augmentation de l'intensité du courant

CAS DU CUIVRE ÉTAMÉ

Modèle : Cuivre étamé

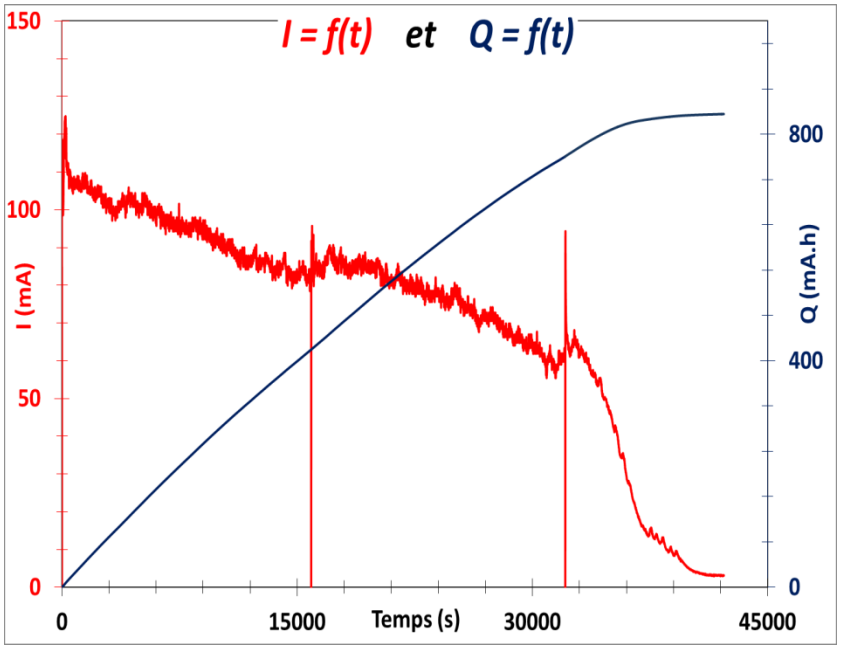
Étain **Cuivre**

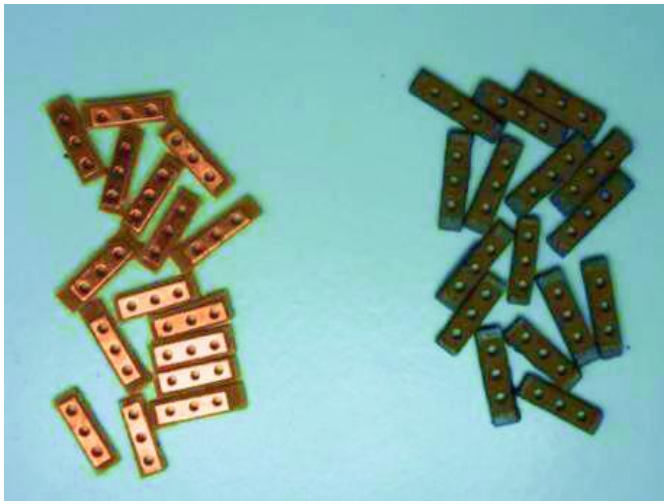
✓ **Étain**

✓ **Cuivre**

Copper balance

Polarized E= 0.35 V Vs SCE

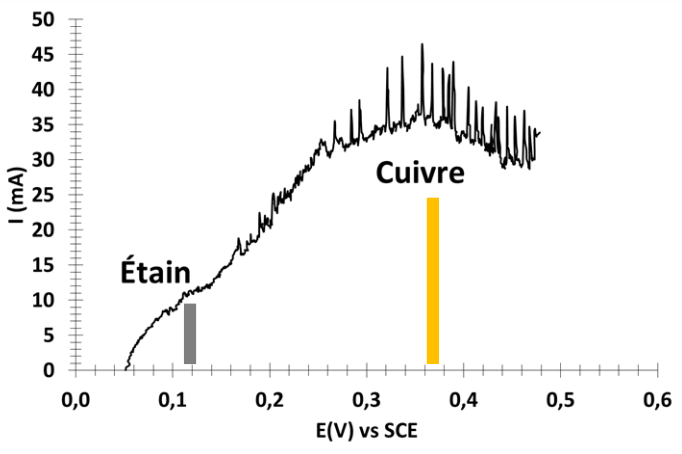


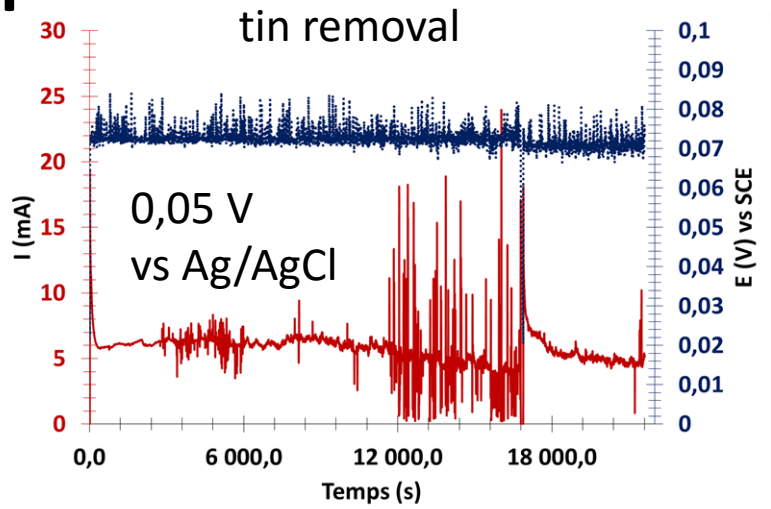


On weighted powder of Cu Faradic yield 95.5 %
Weight change on the counter electrode 90% yield

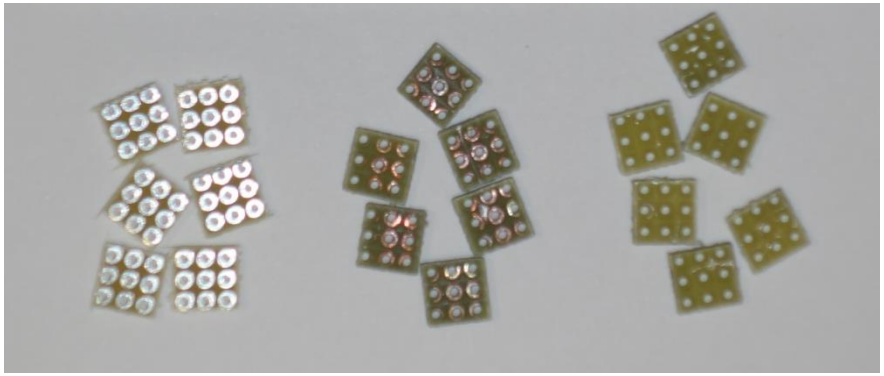
Stripping of Copper on
commercial printed board sold for 35 μm thick copper seems that only 15 μm !

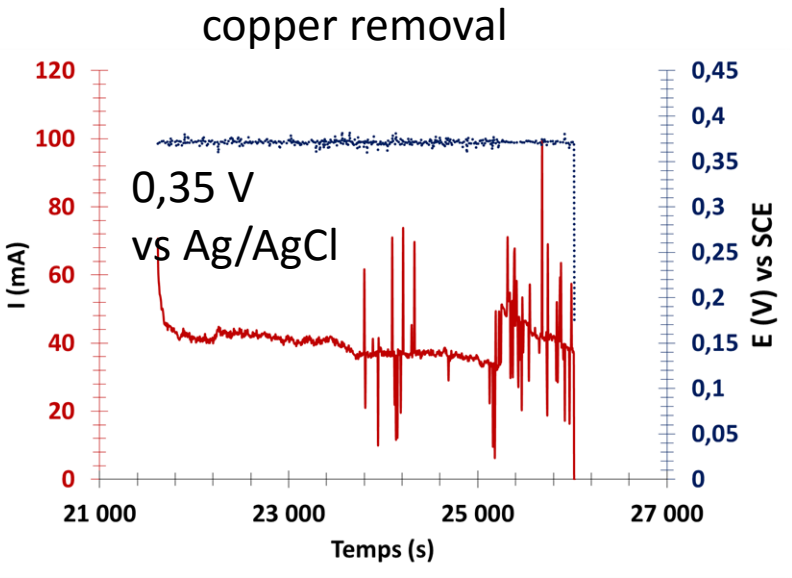
Copper and Tin





Start Sn removed Cu removed



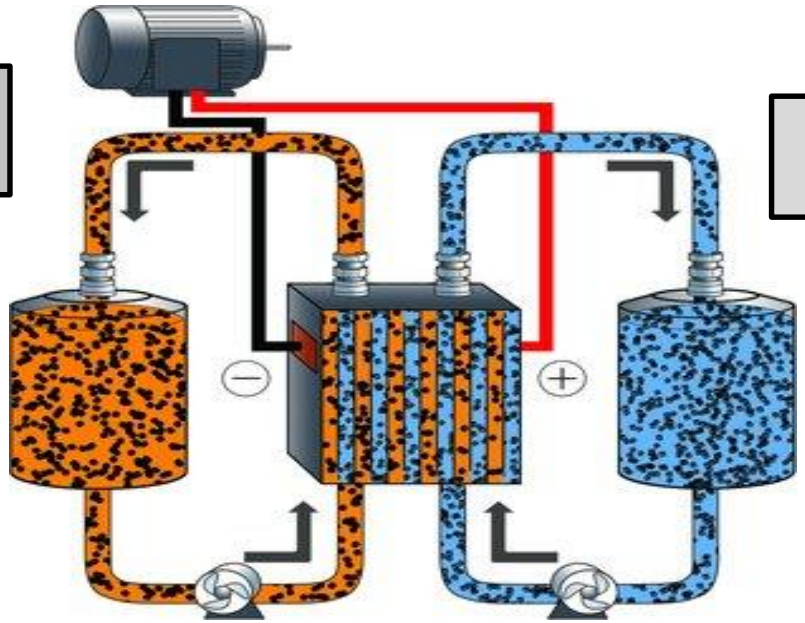


Application II

- Suspension redox flow

$NaTi_2(PO_4)_3$

$Na_{0,44}MnO_2$

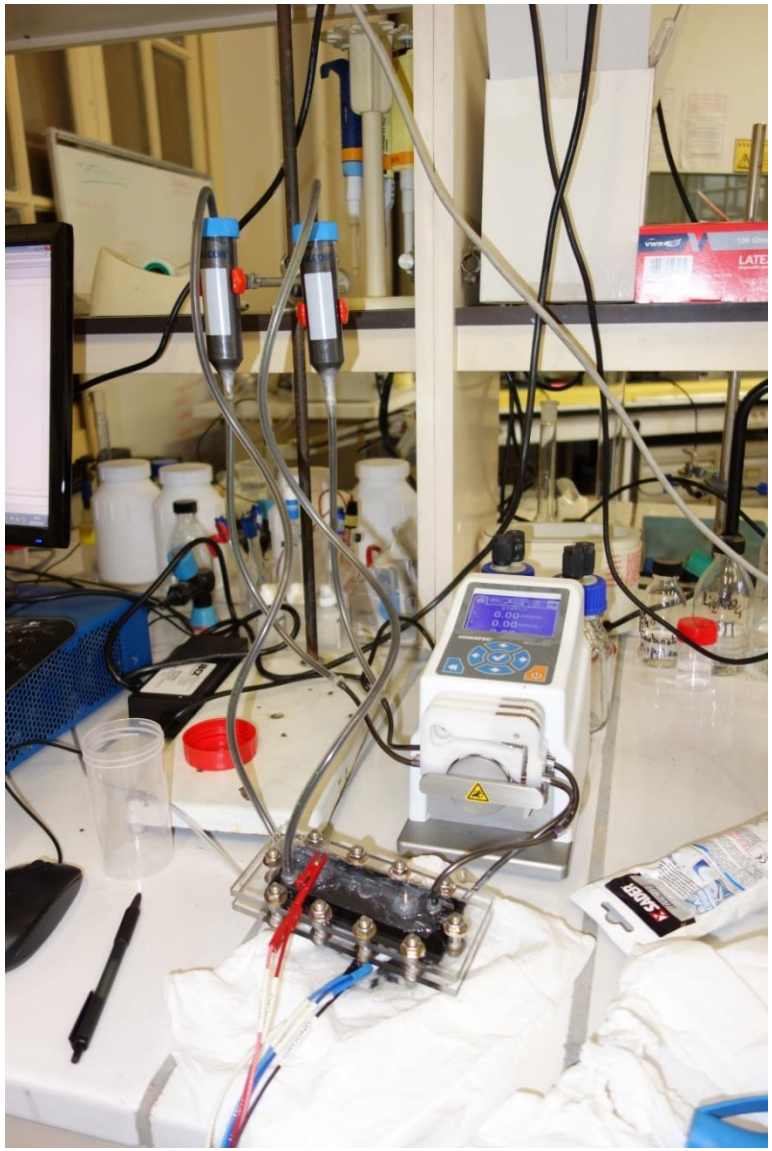


Negative electrode

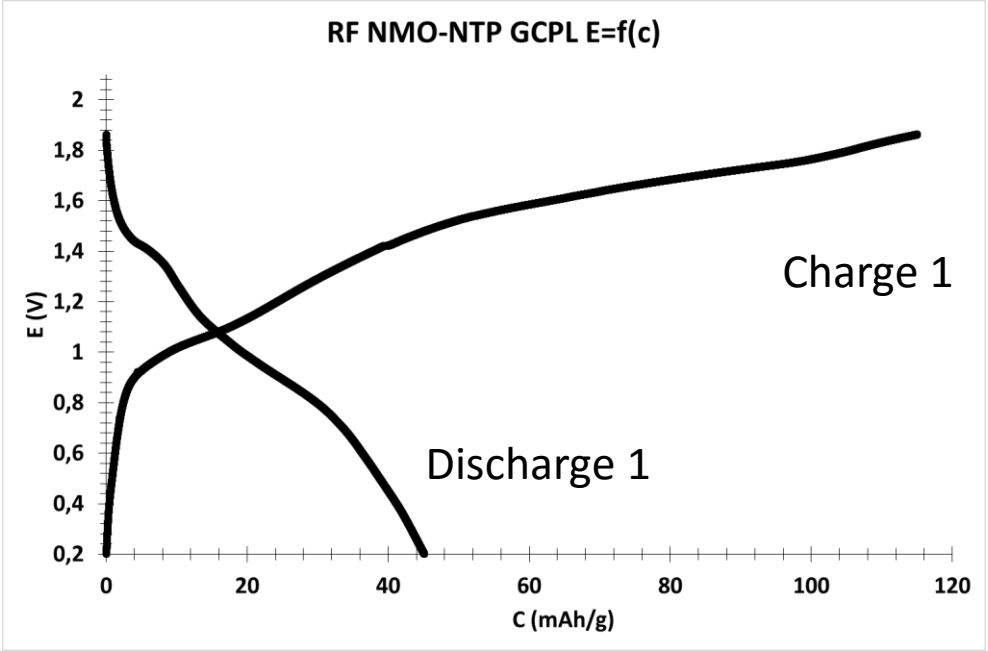
Positive electrode

Redox flow with slurries

Redox flow preliminary demonstration



30mL samples One single cell
21% Graphite can still flow 4 mS/cm electronic
3% active material C/20
$Na_{0.44}MnO_2/KOH/NaTi_2(PO4)_3$



High irreversibility in the first cycle due to $NaTi_2(PO_4)_3$

Conclusions

Thanks support of

Carbon inks conductivity ≈< 10 mS/cm

- Needs to stabilize (plasticizers)
- Needs to texture collectors

Perspectives

optimize the yield and selectivity et la sélectivité Cu/Sn

add Fe^{2+}/Fe^{3+} et complexing agents

include Ag, Au, Pd

addr CN^- or hyposulfite to lower potentials

optimize the pyrolytic steps

Thanks for attention