Silicate appended ionic liquid modified electrodes

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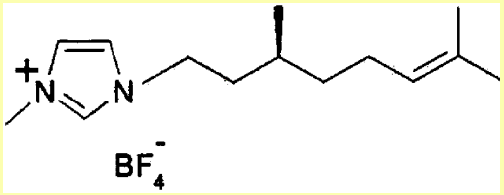
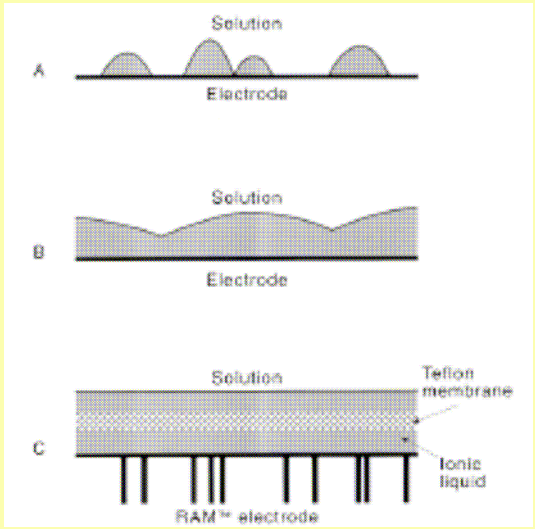
Outline

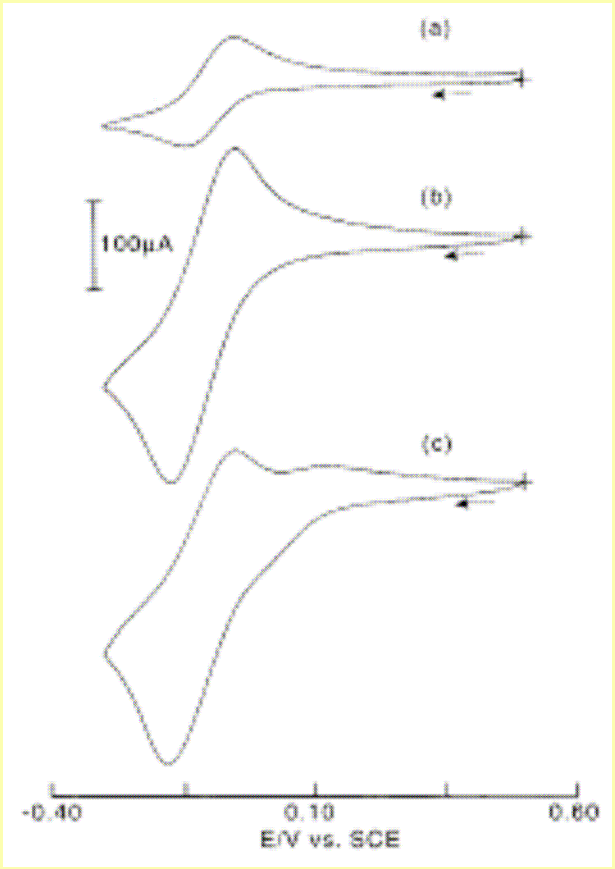
- Introduction (ionic liquid modified electrodes)
- Electrode modified with silicate appended ionic liquid
- Ionic liquid sol-gel precursor for layer by layer electrode film formation
- Conclusions

Introduction
(ionic liquid modified electrodes)

Introduction





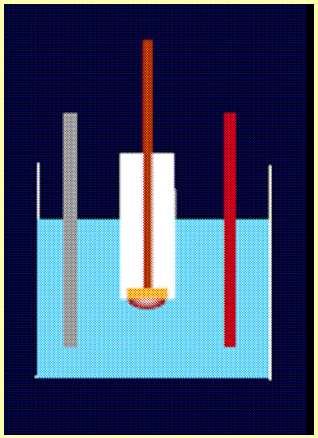


time

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

J. Wadhavan et al. J. Electroanal. Chem. 493 (2000) 75.

Introduction



Electrodes

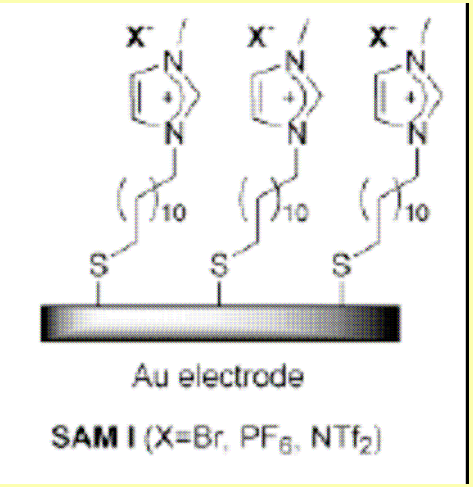
- Electrodes modified with IL drop, droplets or film
- Carbon paste electrodes with IL as a binder
- Electrodes modified with IL-CNT gel
- Multicomponent films or bulk materials with IL as one of the components
- Electrodes modified with thiol appended IL
- Electrodes modified with IL covalently bonded to polymer film √

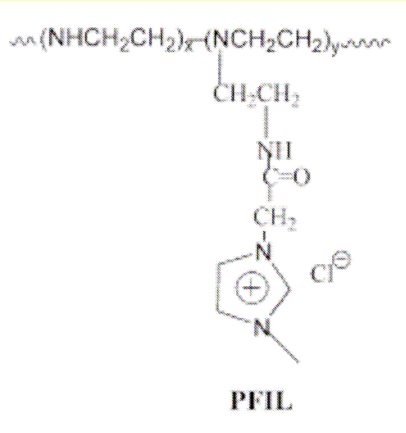
Processes

- Spontaneous ion transfer
- Ion transfer generated by electrochemical redox reaction within IL phase
- Preconcentration of ions or neutral species in IL phase √
- Electrochemical reactions of enzymes immobilised in IL phase
- Electrocatalysis with catalyst present in IL film. Biological systems √
- Electrochemical formation of nanoparticles, polymers or inorganic films

Over 60 papers published until September 2008!!!
(90% in 2006-2008)

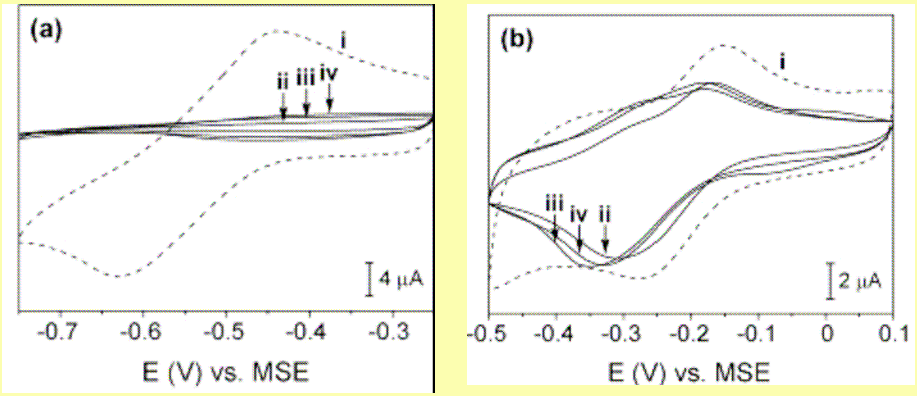
Introduction





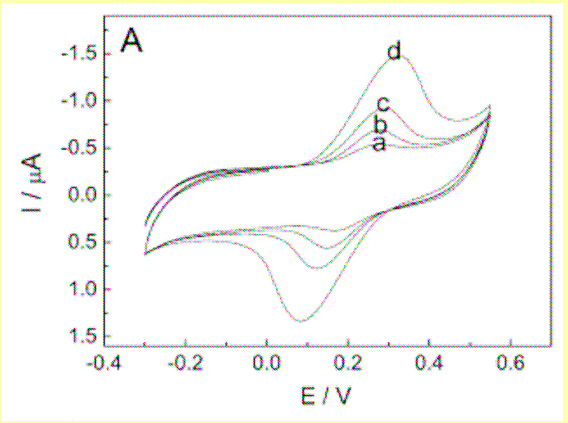
$Ru(NH_3)_6^{3+}$

$Fe(CN)_6^{3-}$



Y. S. Chi et al. Langmuir 21 (2005) 4269.

$Fe(CN)_6^{3-}$



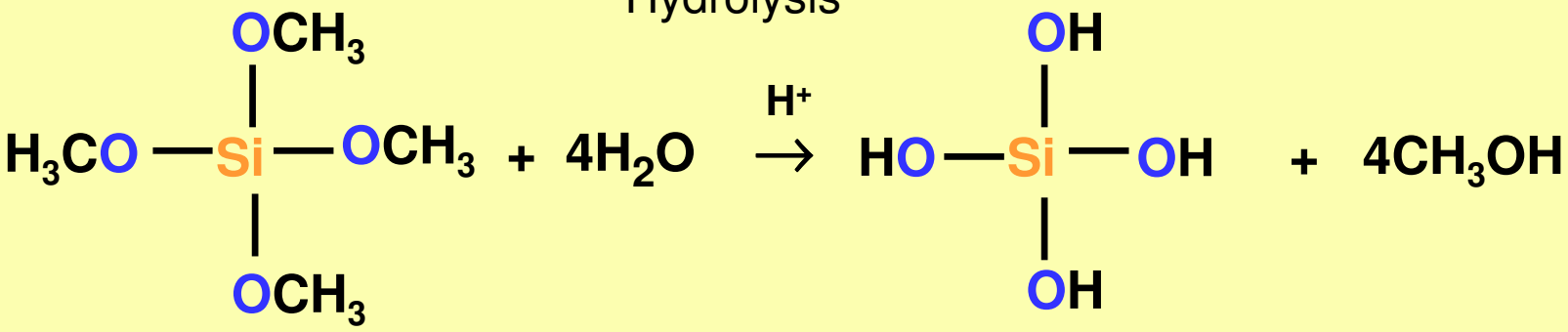
Y. Shen et al. Green Chem. 9 (2007) 2046.

Electrode modified

with silicate appended ionic liquid

Sol-gel process

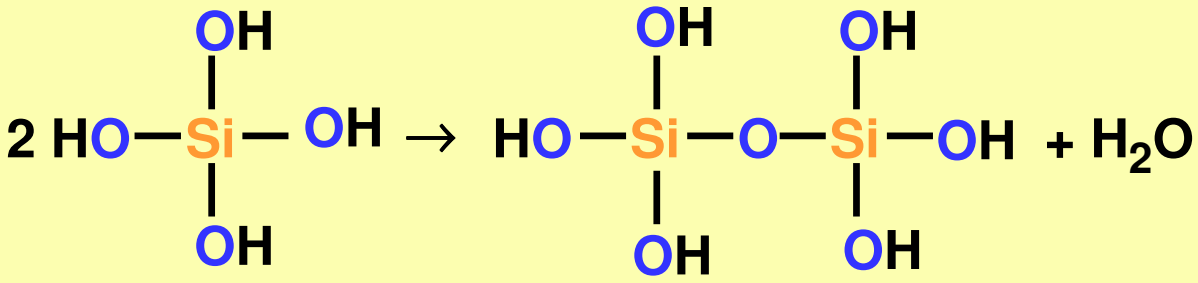
Hydrolysis

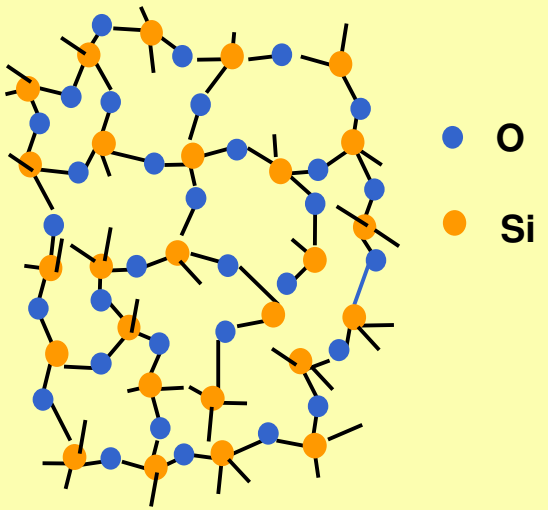


tetramethoxysilane (TMOS)

hydrophilic silicate

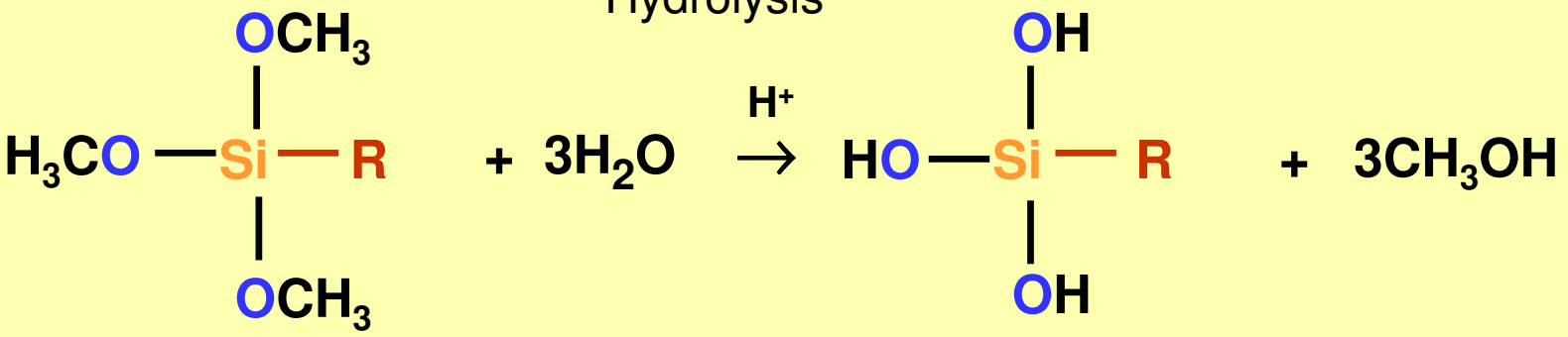
Condensation



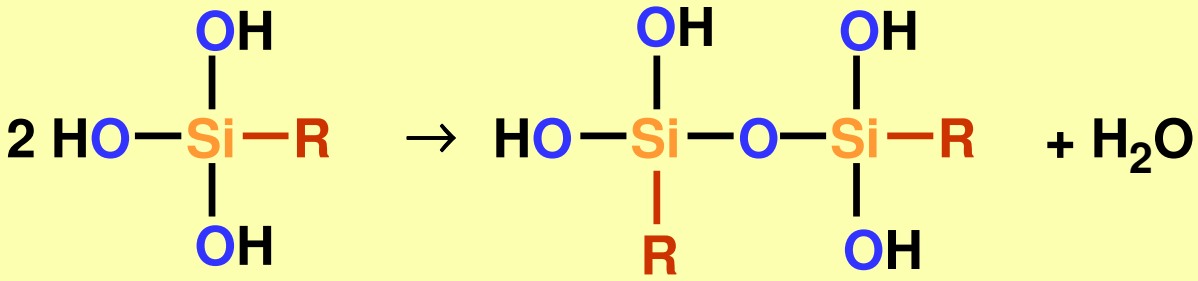


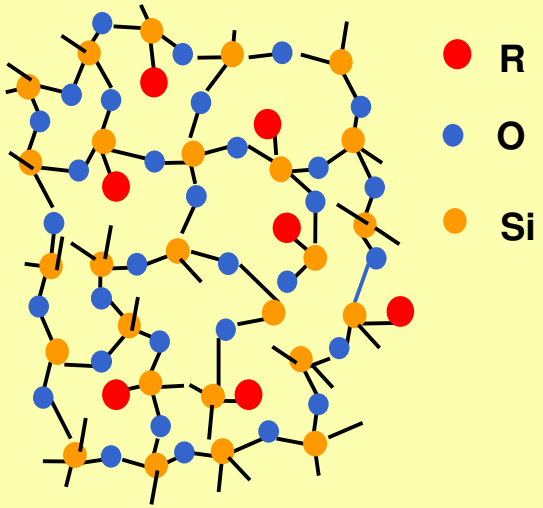
Sol-gel process – substituted silicate

Hydrolysis



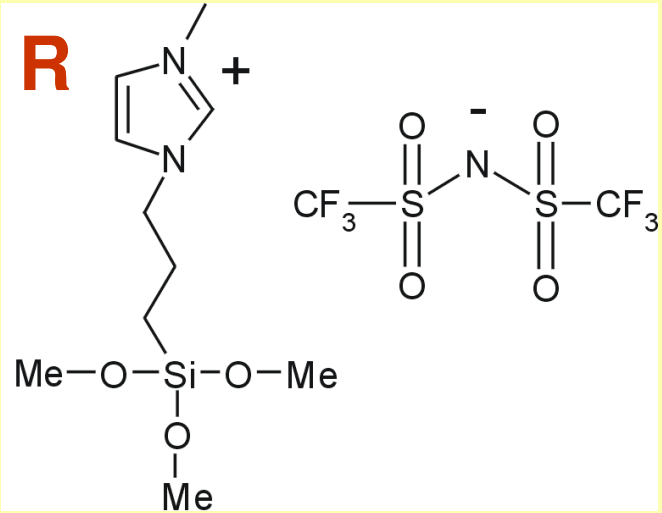
Condensation





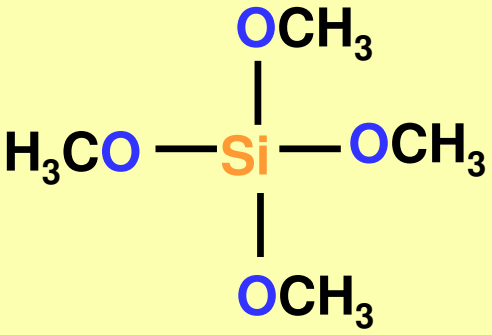
substituted silicate

Electrode modified with silicate appended ionic liquid film

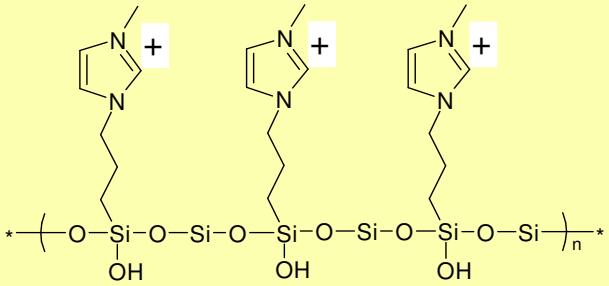


HCOOH - catalyst

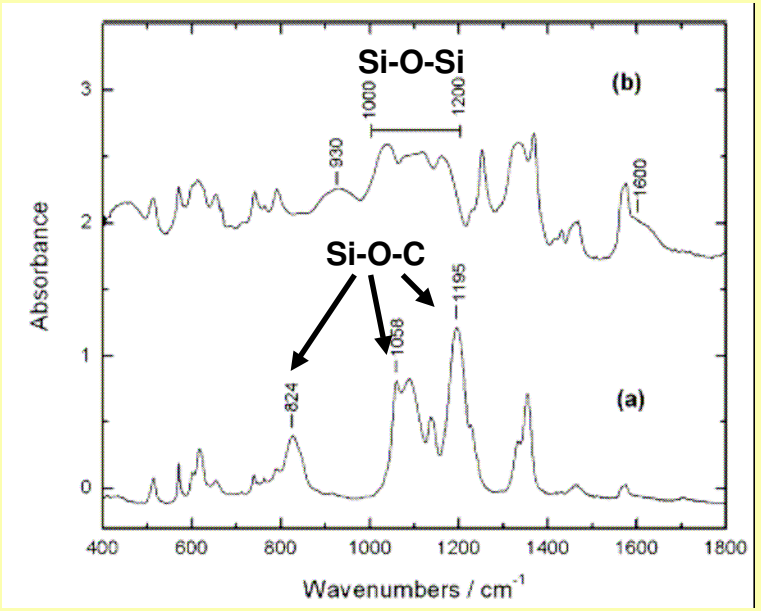
1 : 9



ITO



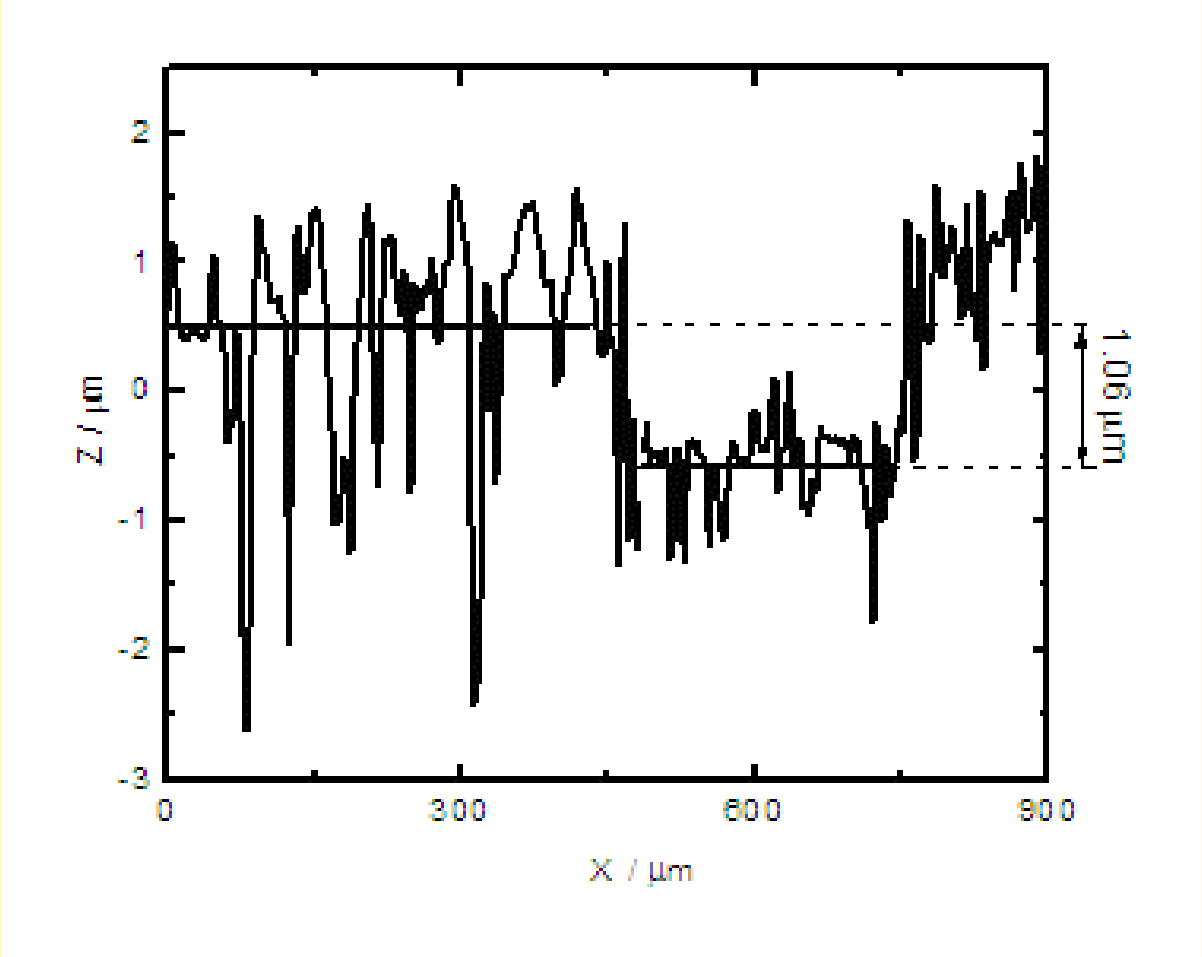
IL appended sol-gel film
Silicate confined ionic liquid



A. Lesniewski et.al. Electrochem. Commun. 9 (2007) 2580

Electrode modified with silicate appended ionic liquid film

Profilometry

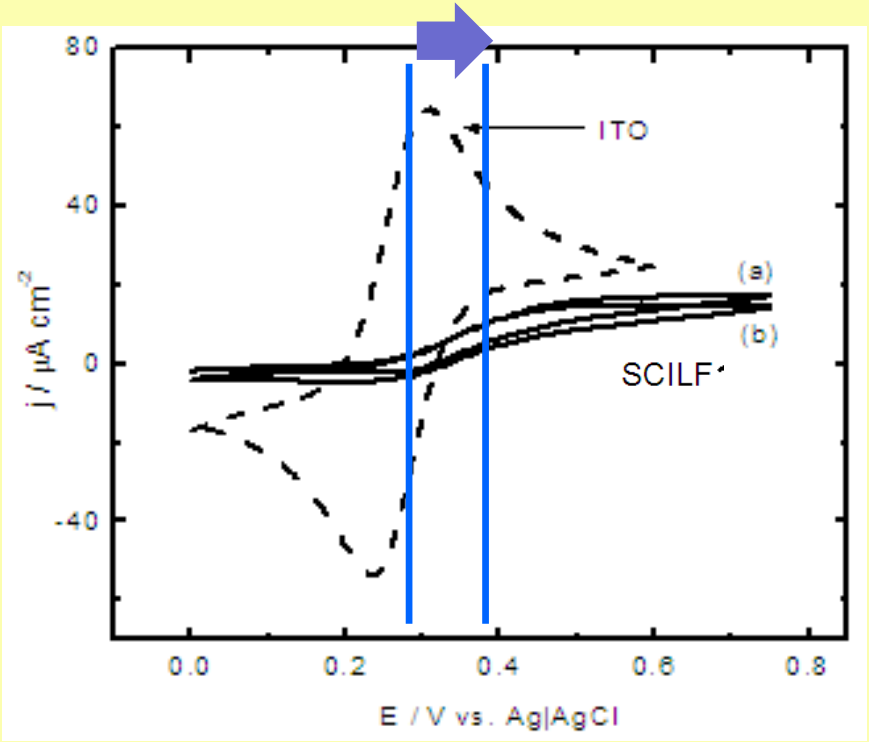


A. Lesniewski et.al. Electroanalysis submitted

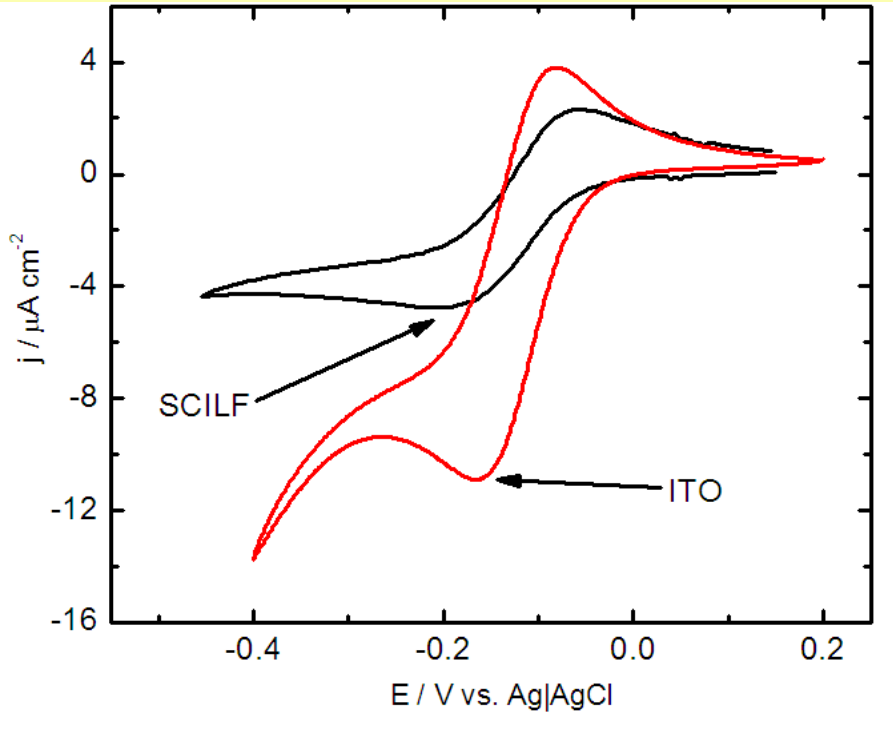
Electrode modified with silicate appended ionic liquid film

Permeability by voltammetry

1 mM **$Fc(CH_2OH)_2$**



0.1 mM **$Ru(NH_3)_6^{3+}$**



$$Fc(CH_2OH)_2 - e \leftrightarrow Fc(CH_2OH)_2^+$$

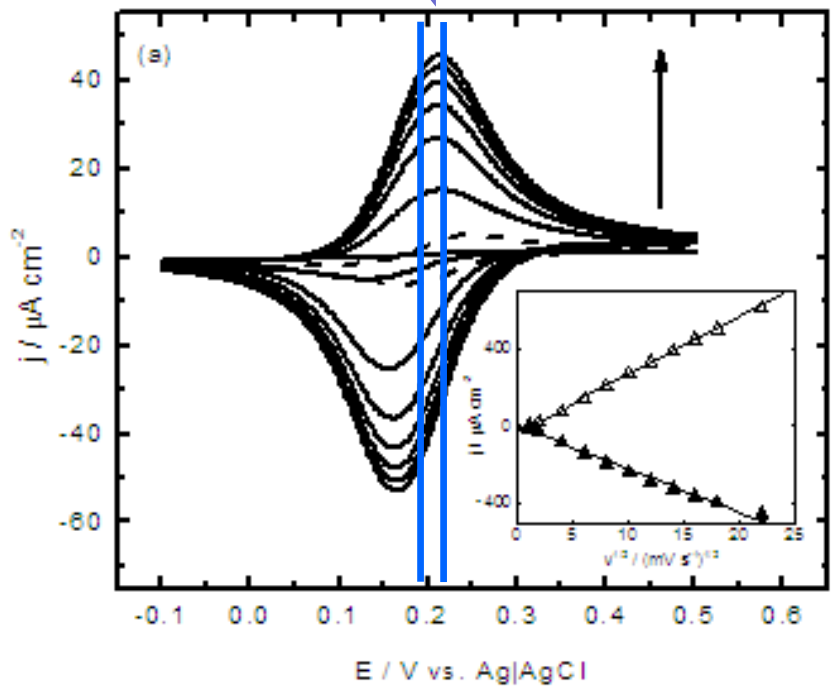
A. Lesniewski et.al. Electroanalysis submitted

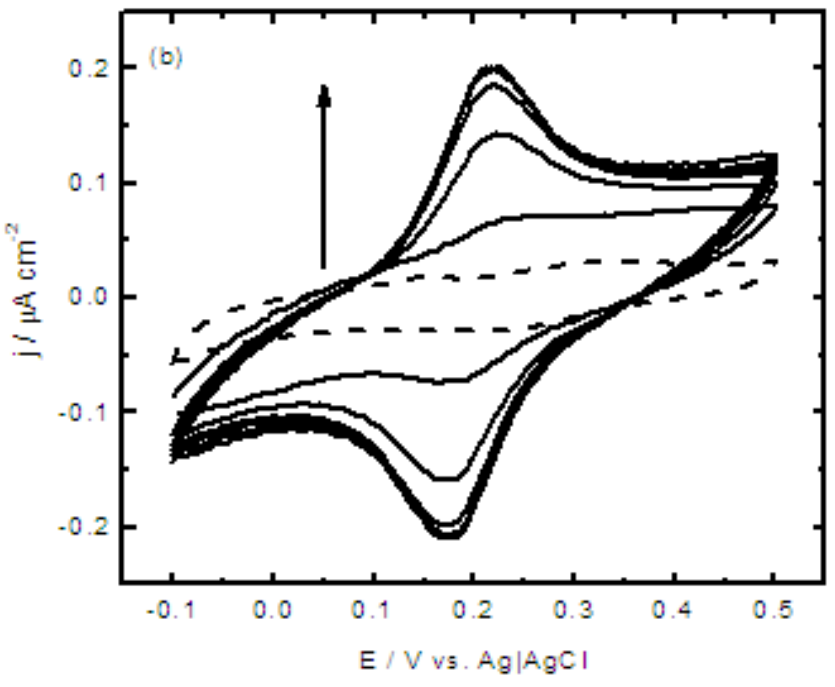
Electrode modified with silicate appended ionic liquid film

Accumulation by voltammetry

0.1 mM $Fe(CN)_6^{4-}$

0.0001 mM $Fe(CN)_6^{4-}$



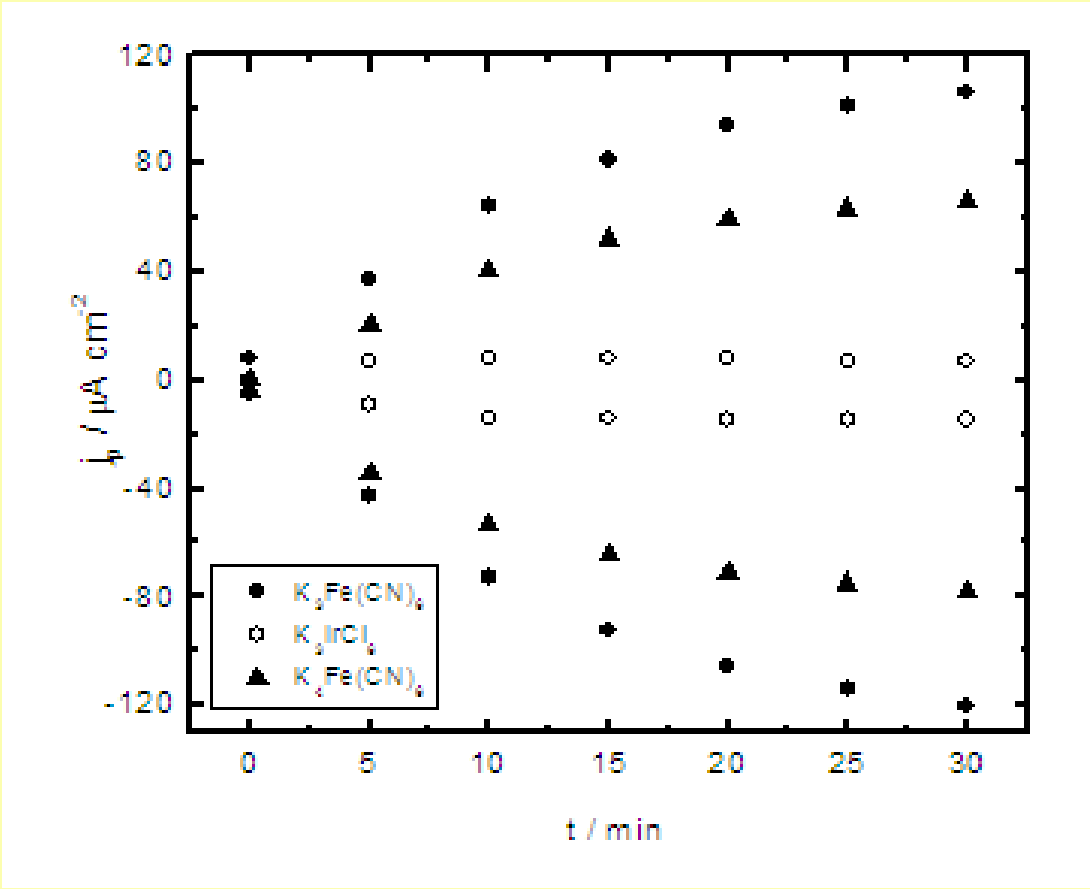


A. Lesniewski et.al. Electroanalysis submitted

Electrode modified with silicate appended ionic liquid film

Accumulation by voltammetry

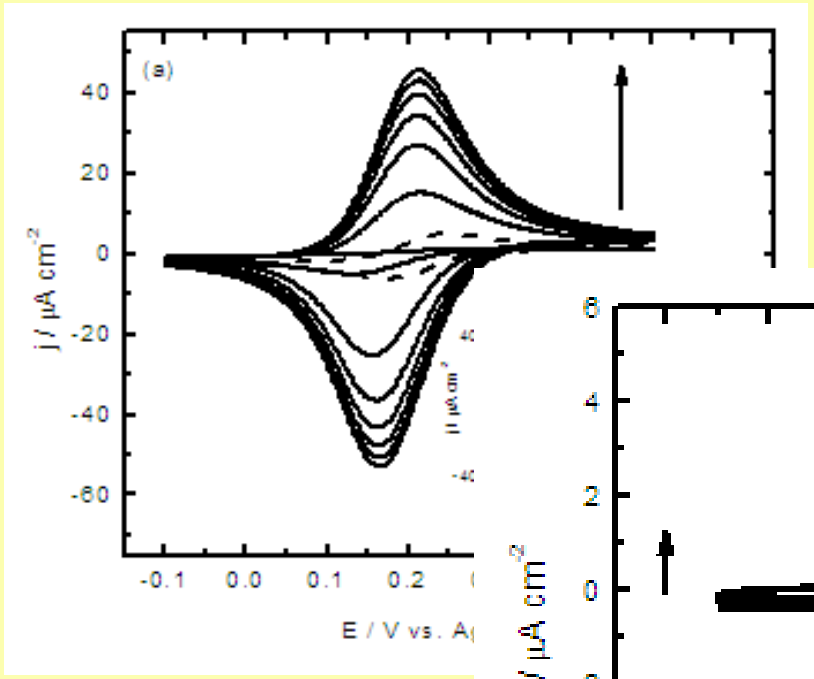
0.1 mM redox probe solution



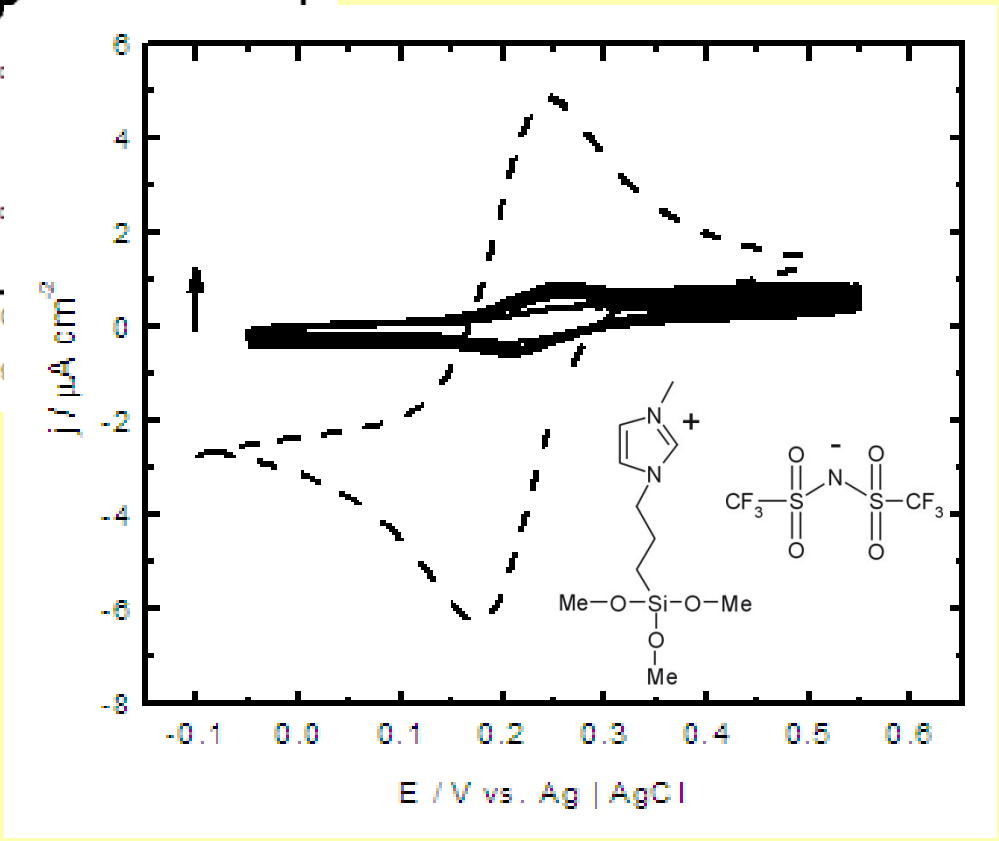
A. Lesniewski et.al. Electroanalysis submitted

Comparison with the electrode modified with ionic liquid precursor

Accumulation by voltammetry

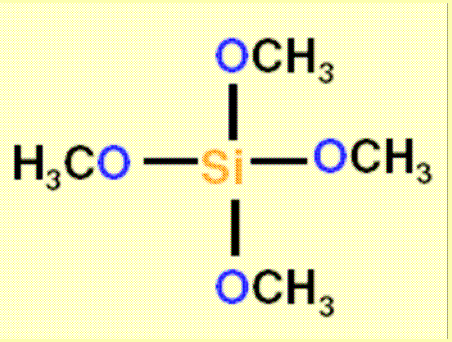


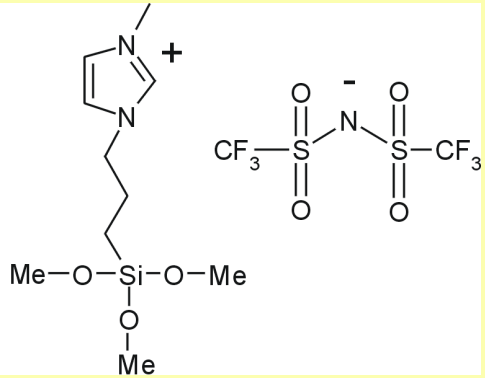
0.1 mM $Fe(CN)_6^{4-}$



A. Lesniewski et.al. Electroanalysis submitted

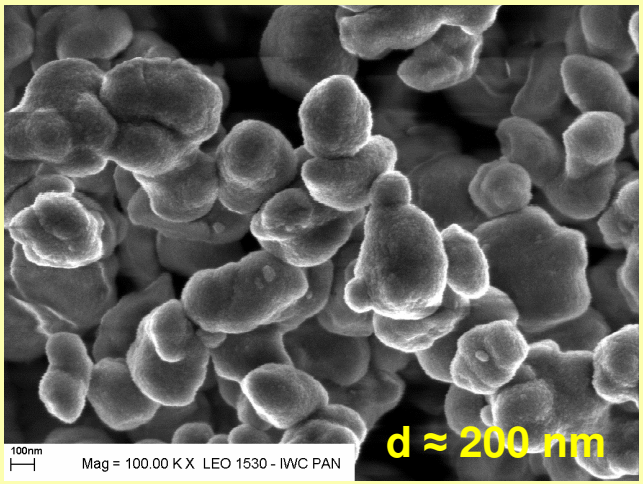
Electrode modified with silicate appended ionic liquid submicroparticles

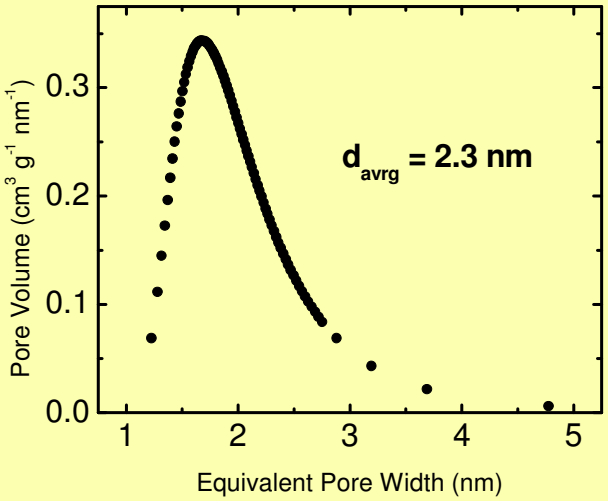




CTAB

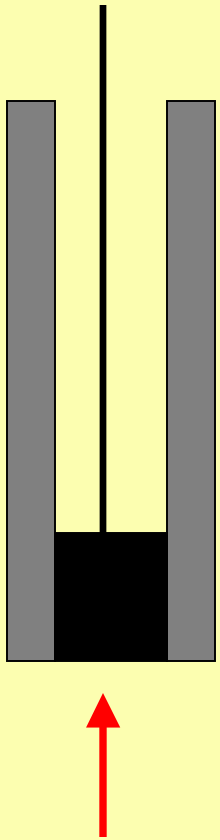
modified Stober method



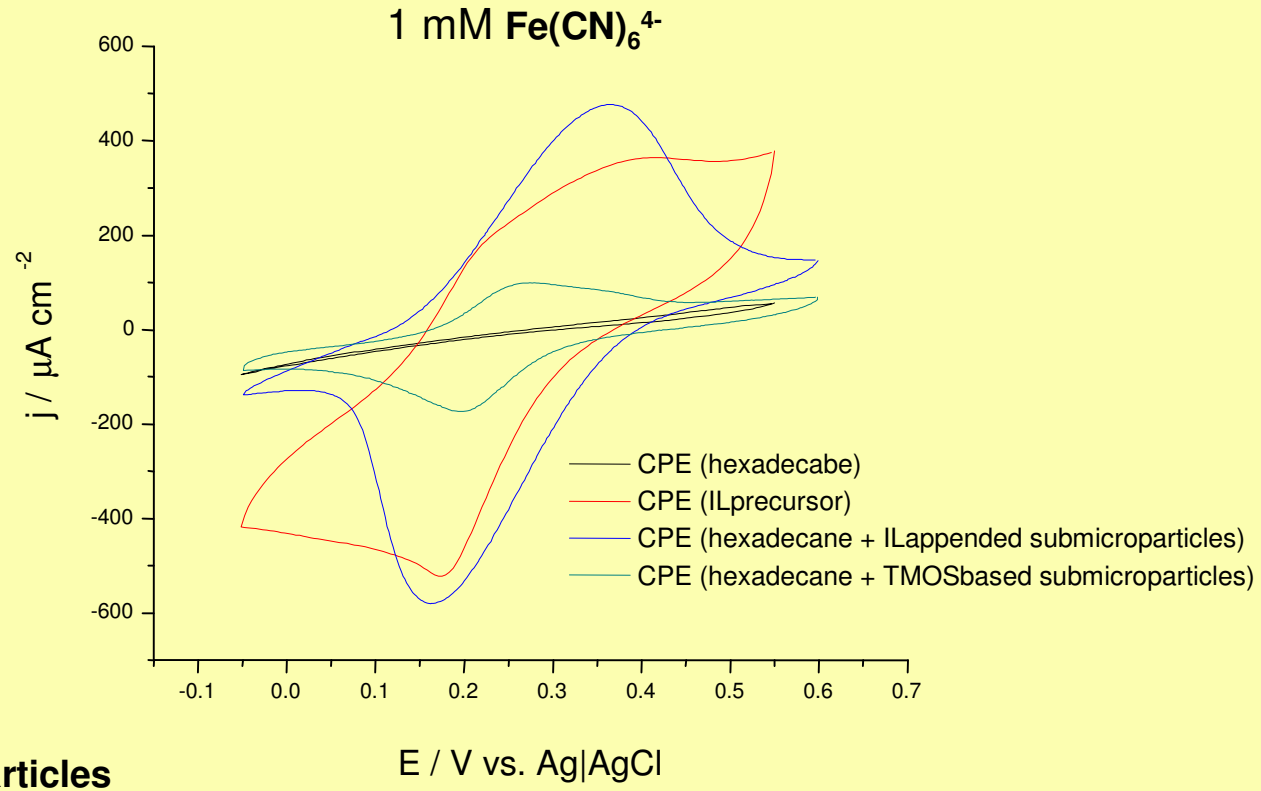


Electrode modified with silicate appended ionic liquid submicroparticles

$Fe(CN)_6^{3-}$ accumulation in CPE modified with submicroparticles

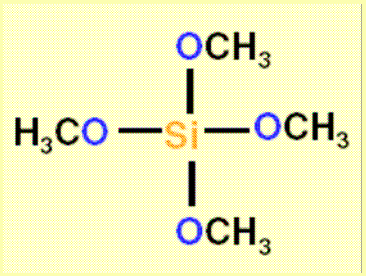


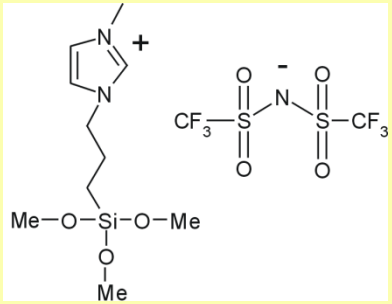
Hexadecane + carbon microparticles
+ IL appended submicroparticles

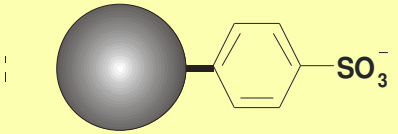


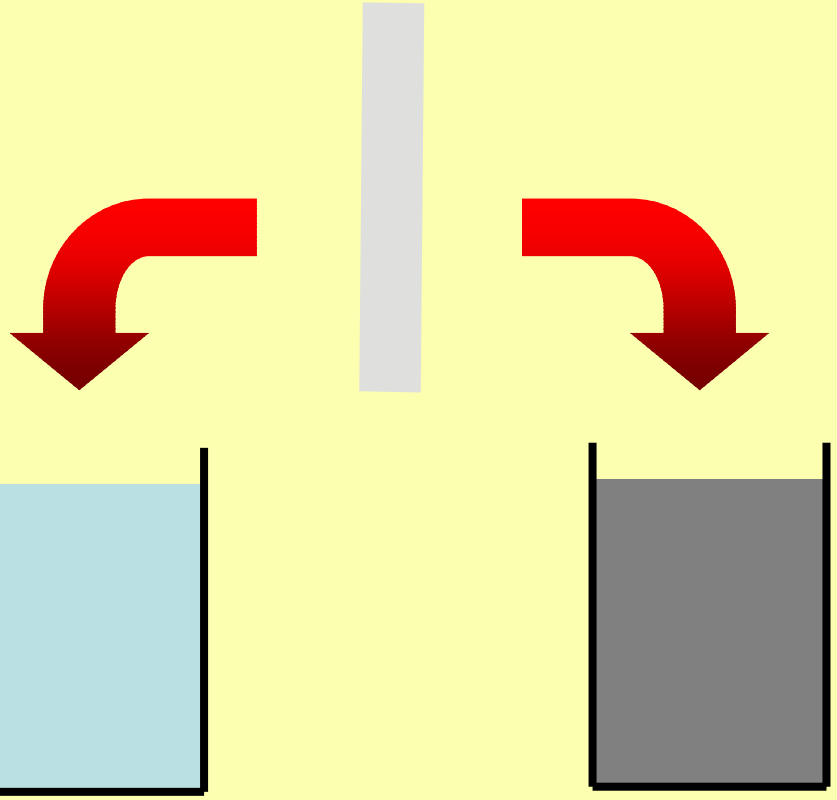
Ionic liquid sol gel precusor for layer by layer electrode film formation

The use of ionic liquid sol gel precusor for layer by layer electrode film formation



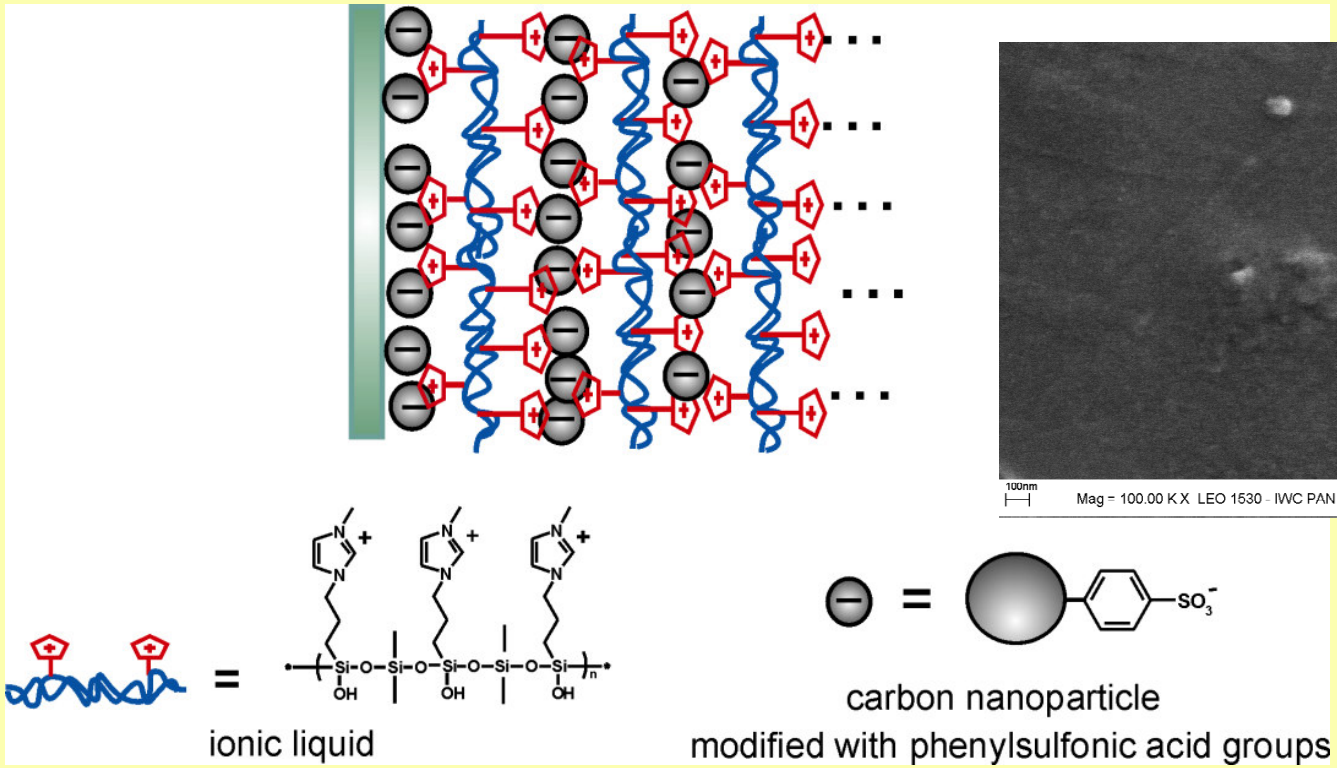






K. Szot et.al. J. Electroanal. Chem. In press

The use of ionic liquid sol gel precusor in layer by layer electrode film formation



maximum 10 layers

the electrostatic self assembly is followed
by the formation of an inorganic polymer network!!!

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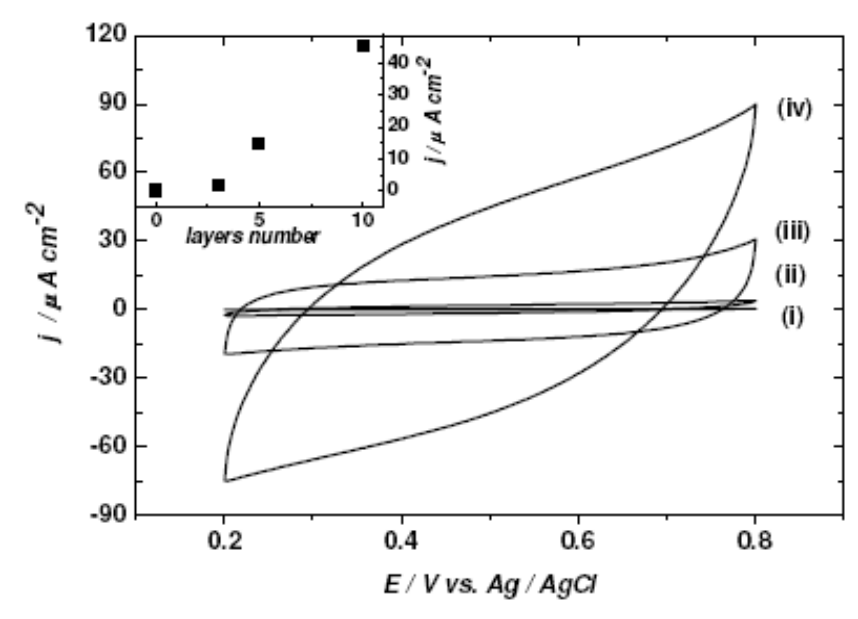
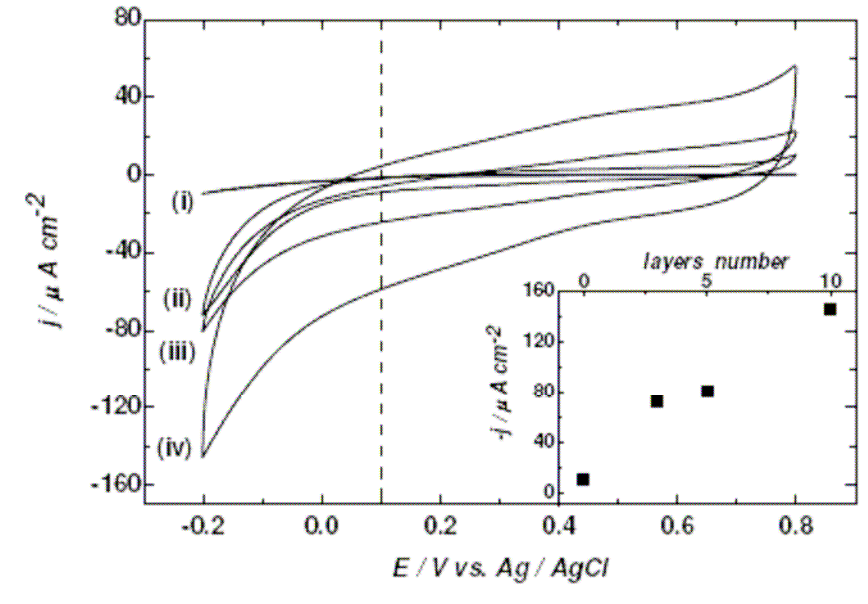
The use of ionic liquid sol gel precusor in layer by layer electrode film formation

(i) ITO		210 Ω
(ii) ITO + 3L	250 nm	230 Ω
(iii) ITO + 5L	690 nm	240 Ω
(iv) ITO + 10L	1060 nm	210 Ω





capacitive current

H_2O_2 electroreduction

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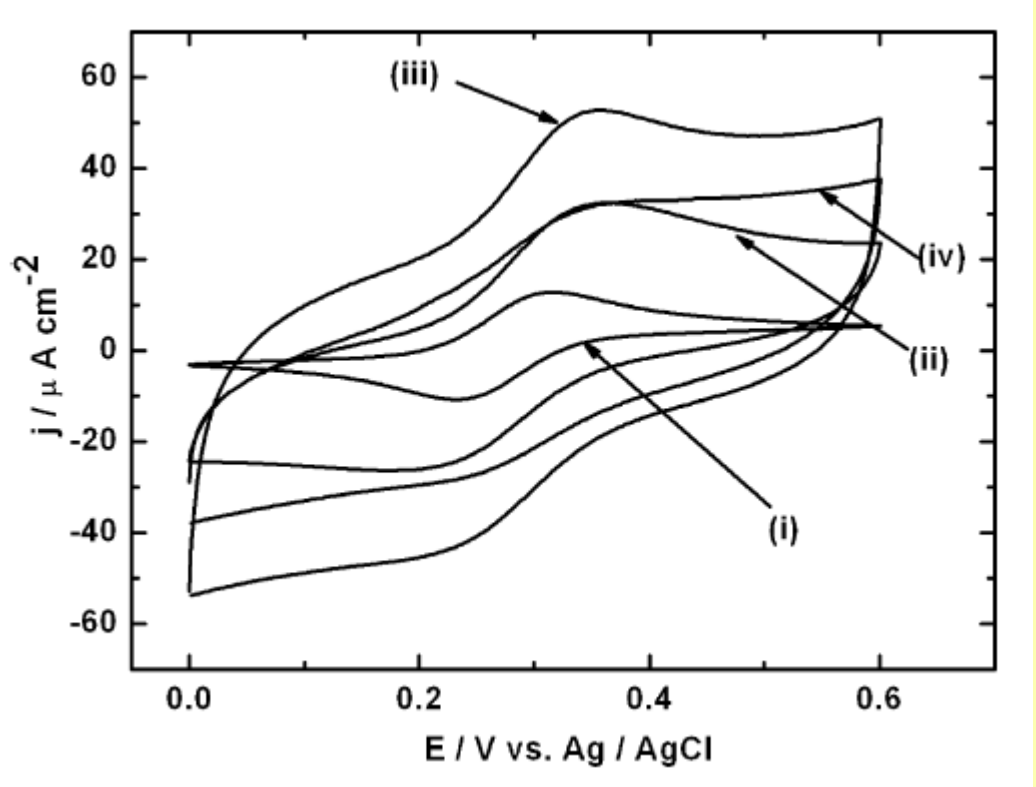
The use of ionic liquid sol gel precusor in layer by layer electrode film formation



(i) ITO
(ii) ITO + 3L
(iii) ITO + 5L
(iv) ITO + 10L

$$Fc(CH_2OH)_2 - e \longleftrightarrow Fc(CH_2OH)_2^+$$

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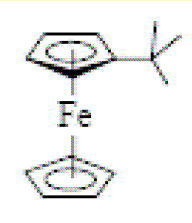
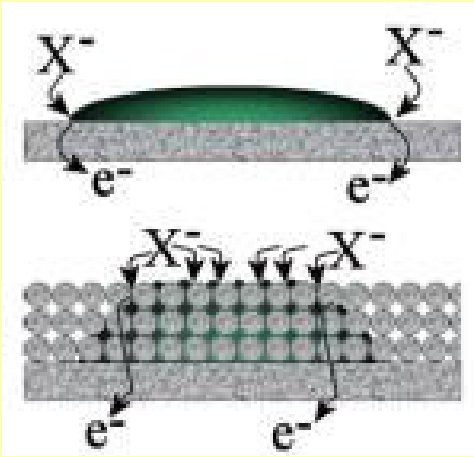
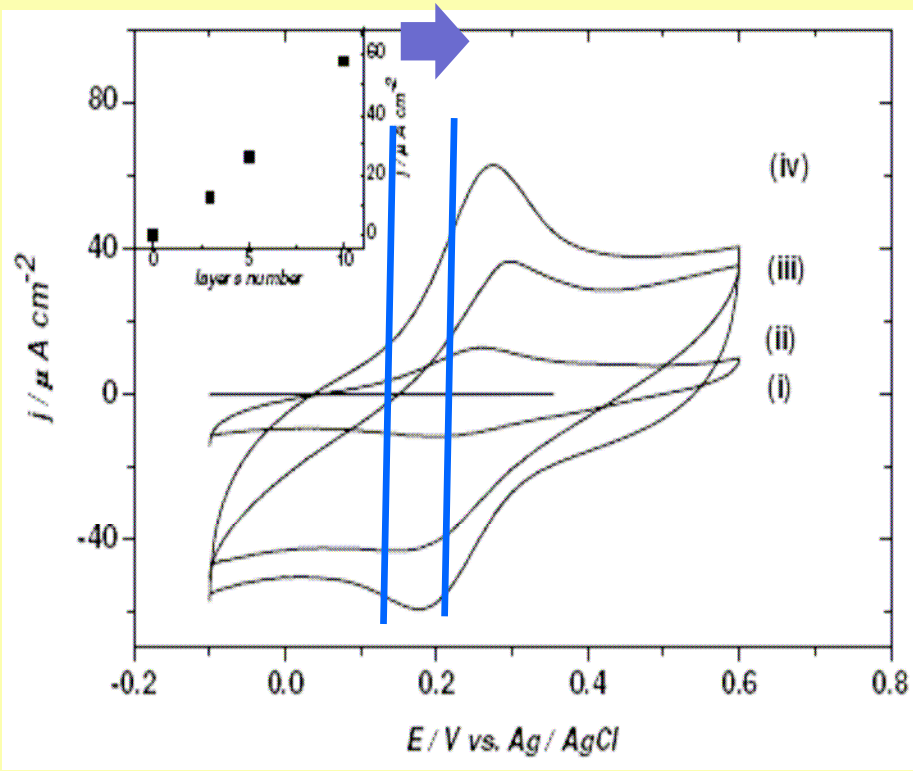
The use of ionic liquid sol gel precusor in layer by layer electrode film formation







(i) ITO
(ii) ITO + 3L
(iii) ITO + 5L
(iv) ITO + 10L

redox liquid (tBuFc) oxidation-reduction

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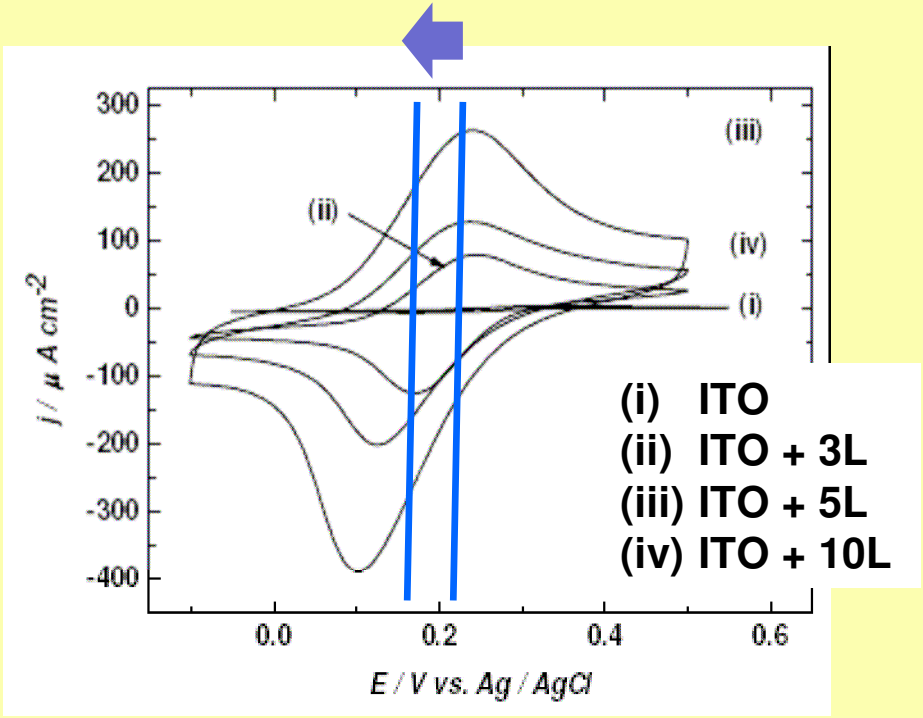
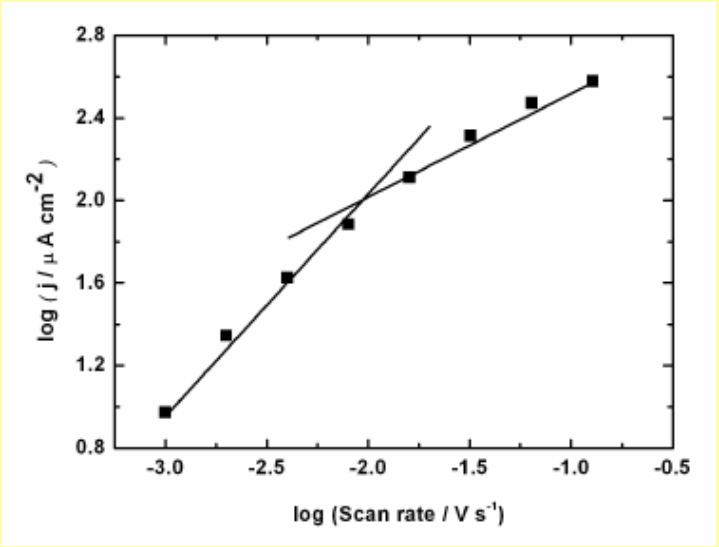
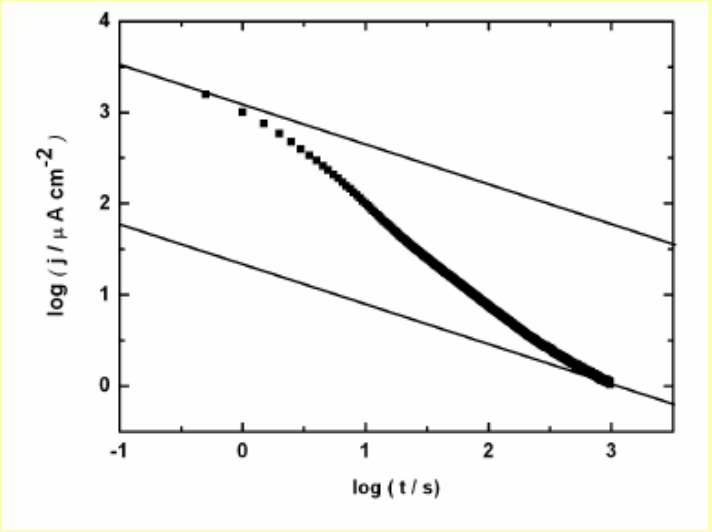
The use of ionic liquid sol gel precusor in layer by layer electrode film formation







$Fe(CN)_6^{3-}$ accumulation
reversible

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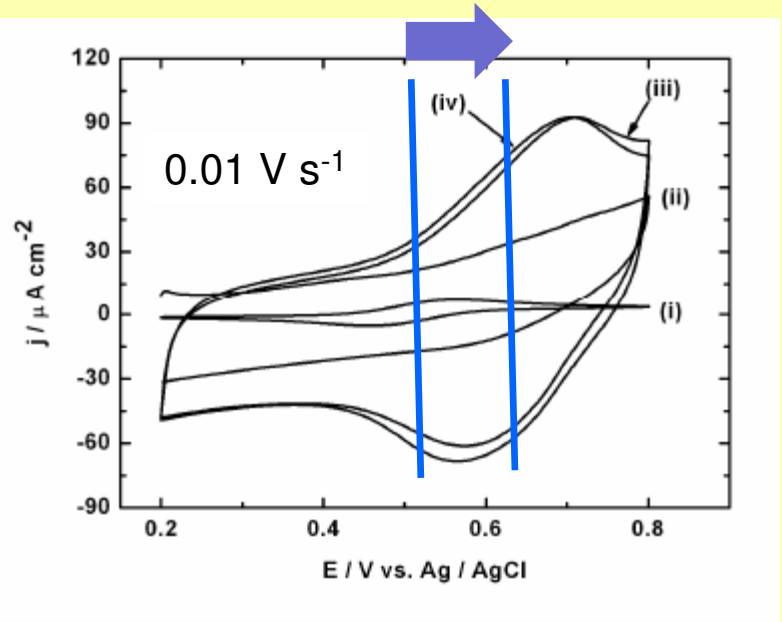
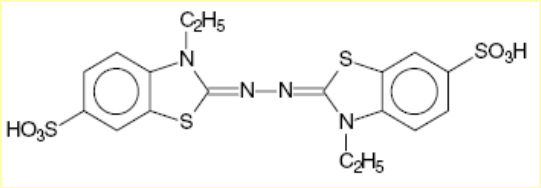
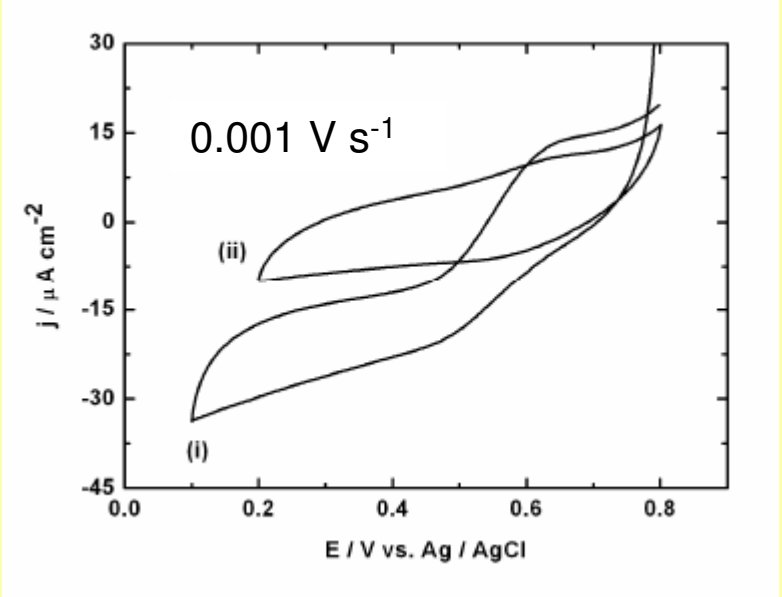
The use of ionic liquid sol gel precusor in layer by layer electrode film formation

(i) ITO
(ii) ITO + 10L, 0 min
(iii) ITO + 10L, 20 min
(iv) ITO + 10L, pure electrolyte



$ABTS^{2-}$ accumulation
irreversible





O_2 reduction catalysis
with laccase in solution

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Acknowledgements

Dr. J. Sirieix-Plenet, dr. C. Rizzi, dr. L. Gaillon (Pierre et Marie Curie Univ , Paris, France)
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Chalmers University of Technology (Goteborg, Sweden)

Ministry of Science and Higher Education (Poland)
project NN204 3687 33 „Electrodes modified with ionic liquids"