

Tamás Pajkossy

- Graduated as a chemist from the Eötvös University, Budapest
- Research worker of HAS institutes
- Teaches (at the TU Budapest) instrumentation of physical chemistry
- Areas of professional interest:
 - semiconductor and polymer electrochemistry (1977-1987)
 - **perturbation methods and related instrumentation (1981-)**
 - connection of electrochemistry and fractal geometry (1983-1990)
 - connection of electrode kinetics and electrode geometry (1983-)
 - double layer properties (1994-)
 - environmental electrochemistry (2004-)
 - electrochemical corrosion problems (1983-)
- **Electrochemical impedance spectroscopy (1982-)**
 - keywords: surface roughness, fractals, adsorption, double layer
 - impedance and roughness (fractality) (1984-1998);
 - **double layer properties of metal electrodes, with and without adsorption effects (1994-);**
 - Frequent participant of the EIA series (Varna, Warsaw, Balaton, Trešt, Rovinj).

Capacitance and potential of zero total charge (*pztc*)
measurements on Au(100) in an ionic liquid, BMIPF₆

Tamás Pajkossy,

Research Centre of Natural Sciences,
Hungarian Academy of Sciences, Budapest,

Soma Vesztergom,
Eötvös University, Budapest,

and

Claus Müller and Timo Jacob
Institute of Electrochemistry, University of Ulm

Capacitance and potential of zero total charge (*pztc*) measurements on Au(100) in an ionic liquid, BMIPF₆

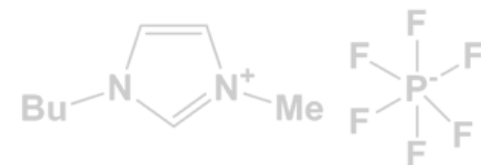
Capacitance: from impedance measurements

pztc: from immersion measurements

Basic properties of the electrochemical double layer

Au(100): well known, simple metal surface

BMIPF₆: pure, well-known ionic liquid



Well-defined model system for metal - ionic liquid interfaces

Basic properties of the electrochemical double layer
of metal - ionic liquid interfaces

Capacitance and potential of zero total charge (*pztc*)
measurements on Au(100) in an ionic liquid, BMIPF₆

Basic properties of the electrochemical double layer
of metal - ionic liquid interfaces

Kinetics of double layer rearrangements
ionic liquids: slow
(aqueous systems: fast – electrostatics governed)

Capacitance and potential of zero total charge (*pztc*) measurements on Au(100) in an ionic liquid, BMIPF₆

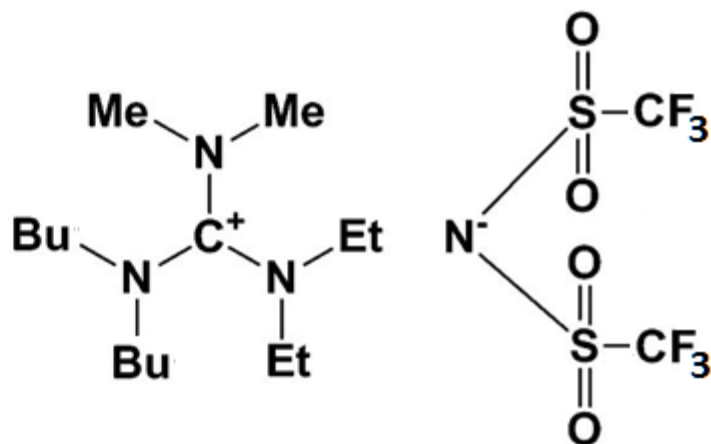
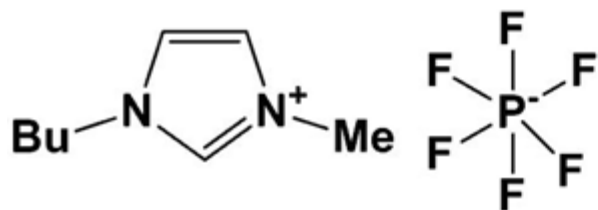
Supporting other measurements with BMITf₂N and N₁₁N₂₂N₄₄GuTf₂N

1-butyl-3-methyl-imidazolium (BMI⁺)

hexafluorophosphate (PF₆⁻)

N,N-dibutyl-N',N'-diethyl-N'',N''-dimethylguanidinium (N₁₁N₂₂N₄₄Gu⁺)

bis(trifluoromethylsulfonyl)imide (Tf₂N⁻)



The aim of the double layer studies: understanding double layer structure ($\Gamma_i(E)$ with cross-sectional distributions) and associated kinetics

Measured quantity: $i(t)$ as function of $E(t)$ – CV ($i(t, E(t))$), EIS($Z(\omega)$)

Provided that we can get rid of (or separate) Faradaic currents

Step 1: $i(t, E(t))$ or $Z(\omega) \rightarrow C = dq^M/dE$

Provided that we know pztc $\equiv E(q^M=0)$

Step 2: $C(E) \rightarrow q^M(E);$

Provided that we know electrosorption valencies (formal charge transfer numbers) $\gamma_i = (-1/F) dq^M/\Gamma_i$

Step 3: $q^M(E) \rightarrow \Gamma_i(E) \quad \Gamma_i(E) = -1/(\gamma_i F) dq^M(E)$

can be calculated.

The aim of the double layer studies: understanding double layer structure ($\Gamma_i(E)$ with cross-sectional distributions) and associated kinetics

Measured quantity: $i(t)$ as function of $E(t)$ – CV ($i(t, E(t))$), EIS($Z(\omega)$)

Provided that we can get rid of (or separate) Faradaic currents

Step 1: $i(t, E(t))$ or $Z(\omega) \rightarrow C(\omega)$

Provided that we have a model for the kinetics

Step 2: $C(\omega) \rightarrow$ rates, rate coefficients can be calculated.

**impedance &
capacitance**

Electrochemical impedance spectroscopy: for characterizing charged interfaces (double layers) and determining rates

Measurement: in equilibrium or in steady state

Stimulus: $E(t) = E_{dc} + E_{ac} \sin(\omega t)$

Response: $I(t) = I_{dc} + I_{ac} \sin(\omega t + \varphi)$

Impedance:

- is a complex quantity defined as

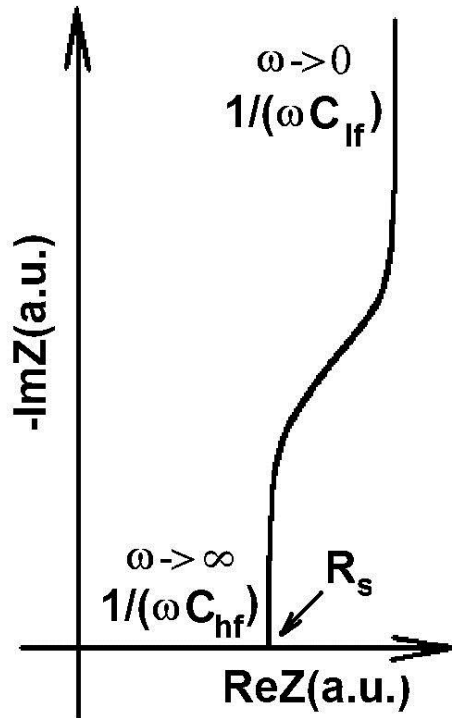
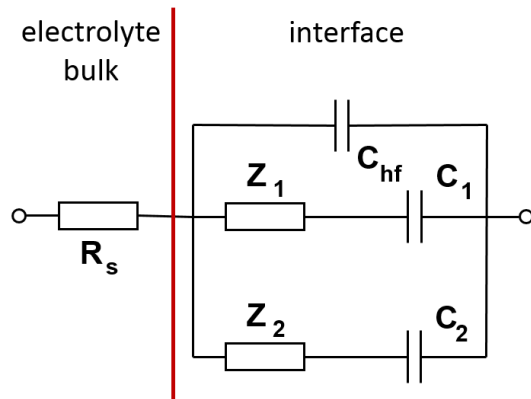
$$Z \equiv Z_{abs} \exp(i\varphi) = Z_{abs} \cos \varphi + i \cdot Z_{abs} \sin \varphi \text{ with } Z_{abs} \equiv E_{ac} / I_{ac}$$

- is a spectrum (typically $1 \text{ mHz} < f < 1 \text{ MHz}$);
- is usually interpreted in terms of equivalent circuits of R, C and other (e.g. W: diffusional impedance) elements.

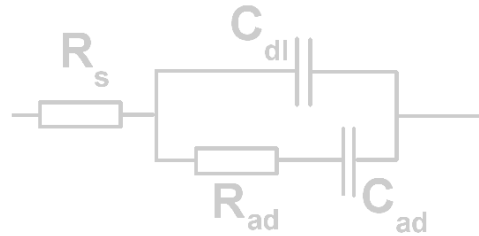
Information obtained: d/dE of

- surface charge (=double layer and adsorption capacitances)
- rates of Faradaic and non-Faradaic processes

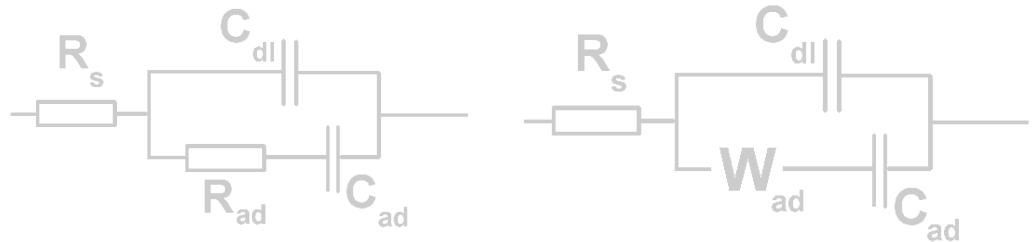
Impedance of a „blocking” electrode („absence of Faradaic reactions”)



Origin: adsorption impedance theory for a binary electrolyte



Dolin & Ershler (hydrogen adsorption, 1940)



Frumkin & Melik-Gaykazyan (adsorption of a minor component, with supporting electrolyte, 1951)

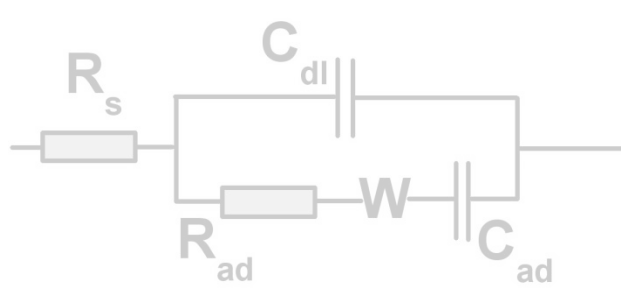
For easier visualization $Z(\omega)$ is transformed to $C(\omega)$ as

$$C(\omega) = \frac{Y_{if}(\omega)}{i\omega} = \frac{1}{i\omega(Z(\omega) - R_s)}$$

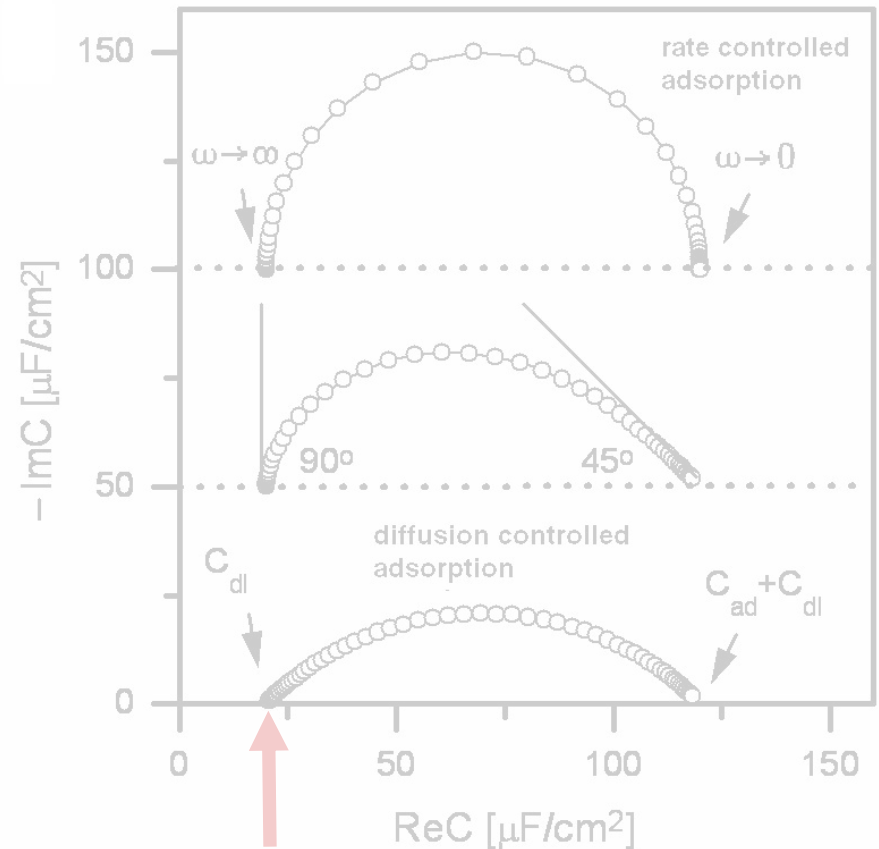
where

- ω : frequency; i : imaginary unit
- $Z(\omega)$: measured impedance spectrum
- $R_s = Z(\omega \rightarrow \infty)$
- $C(\omega)$: (complex) capacitance spectrum

$C(\omega)$ of



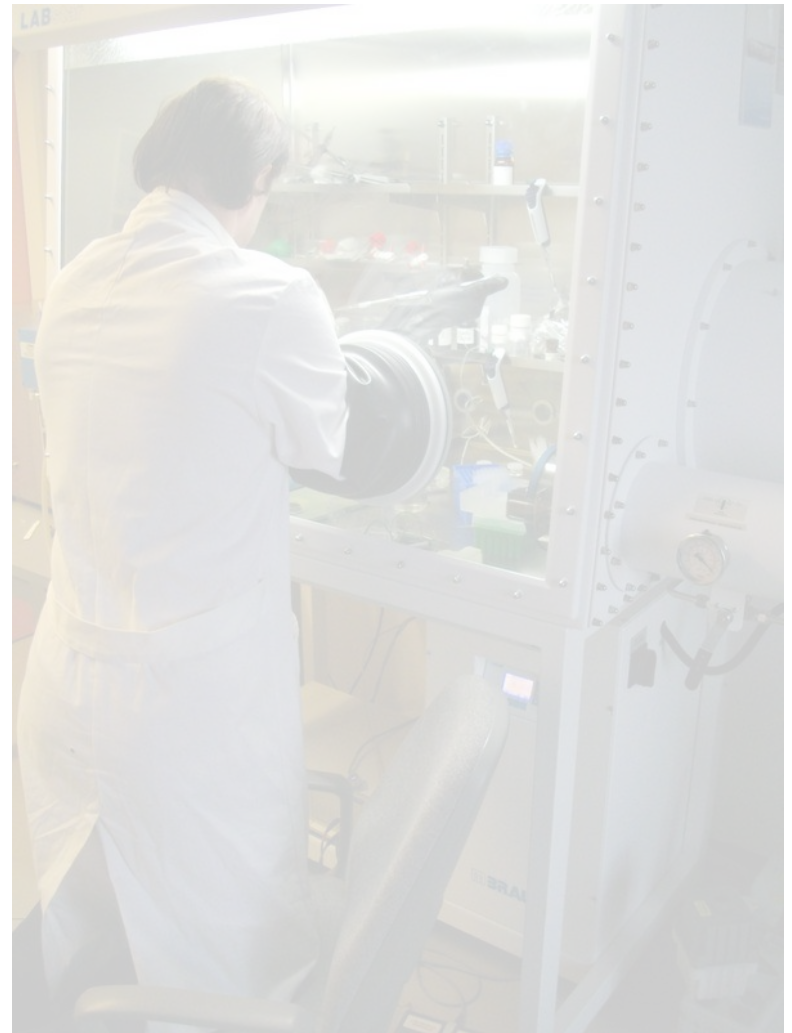
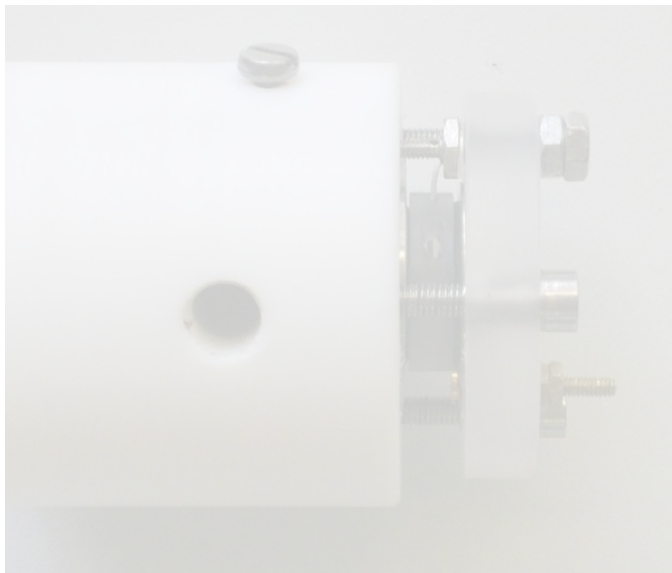
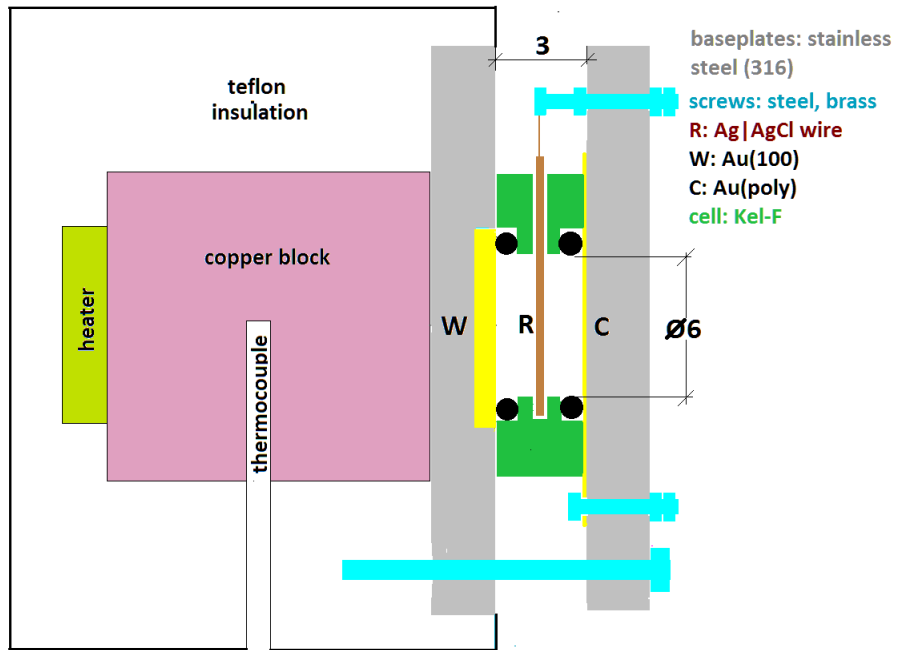
$$C(\omega) = C_{dl} + \frac{C_{ad}}{1 + \sigma_{ad} C_{ad} \sqrt{i\omega} + R_{ad} C_{ad} i\omega}$$



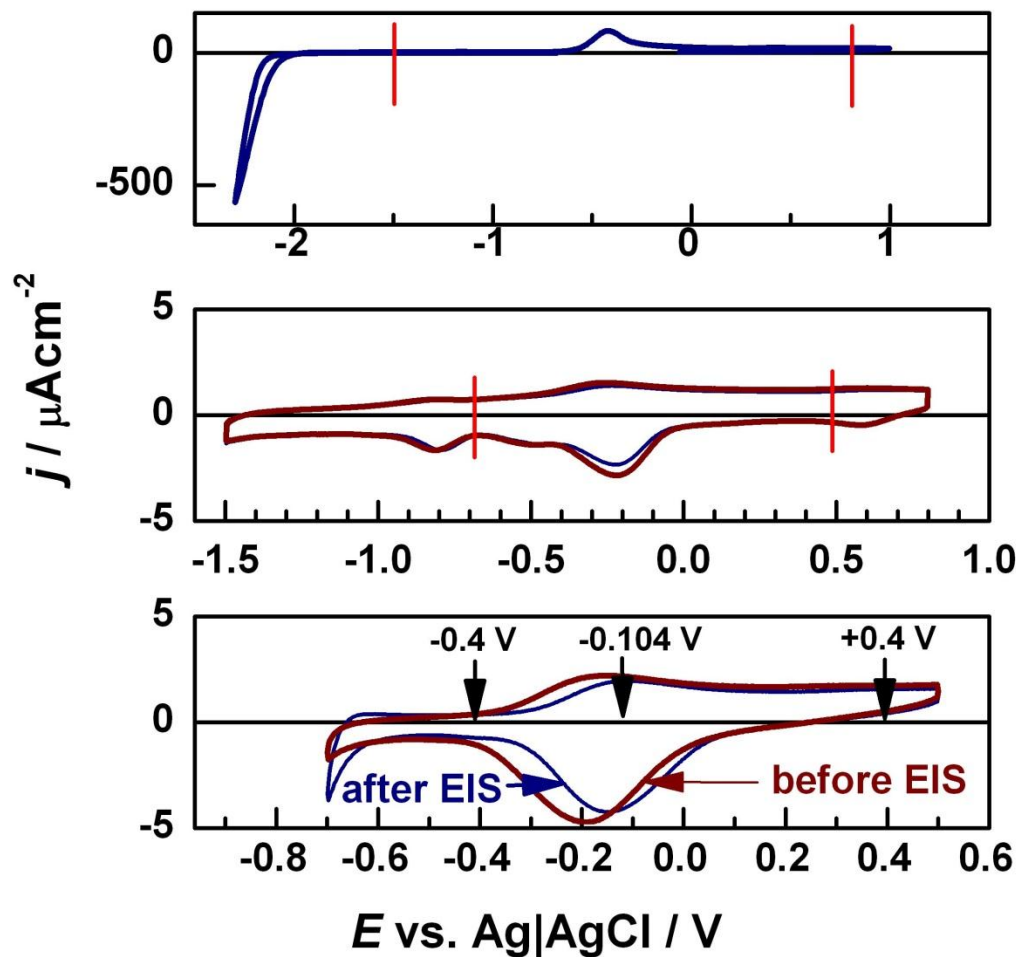
$$C_{dl} = C(\omega \rightarrow \infty)$$

Points shift clockwise
with increasing c_{ad}

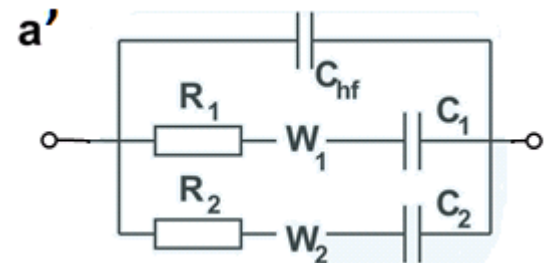
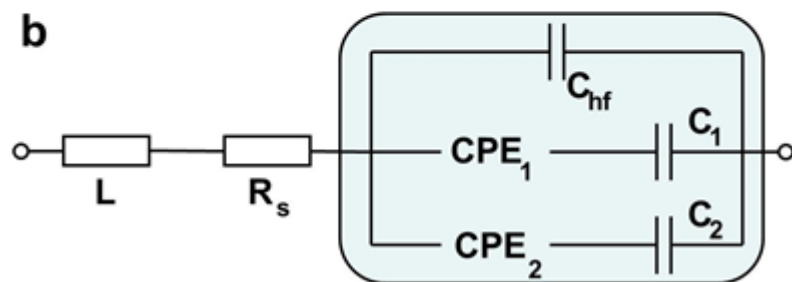
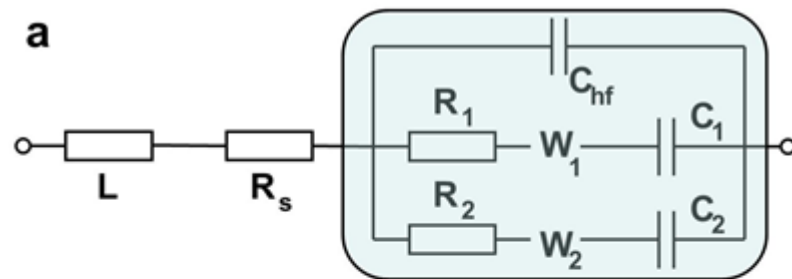
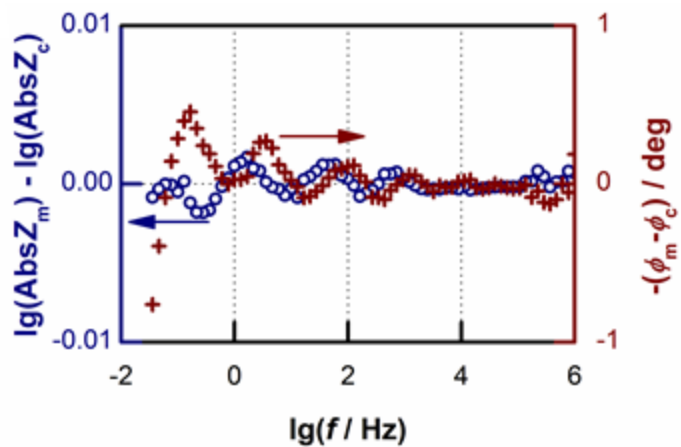
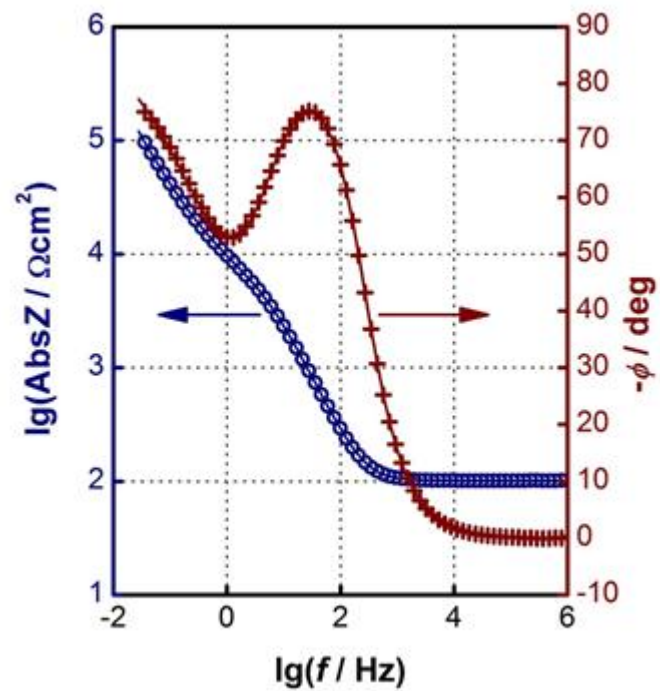
Experimental:

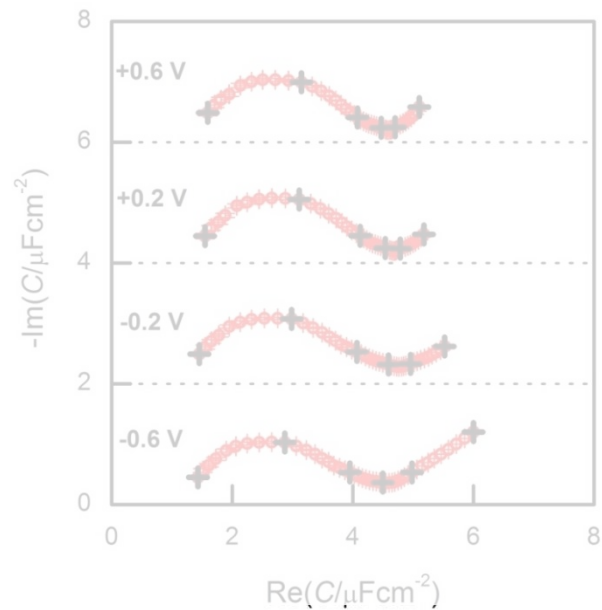
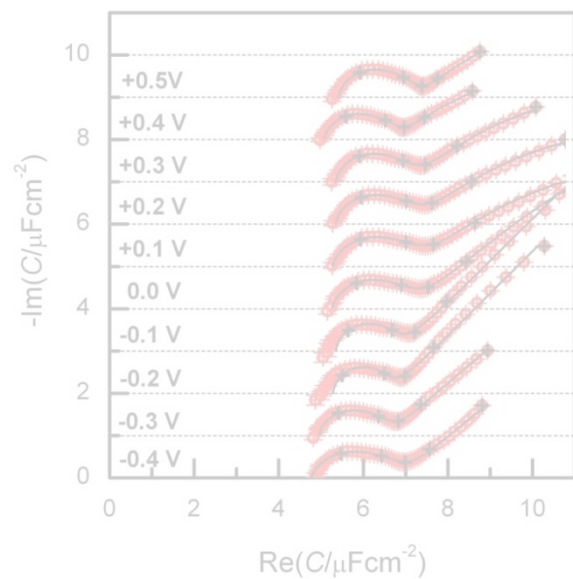
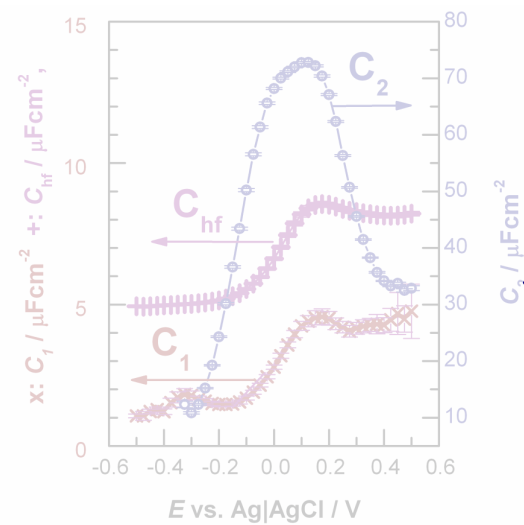
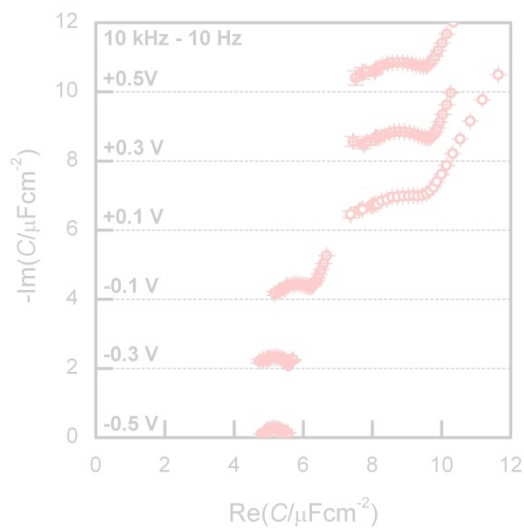
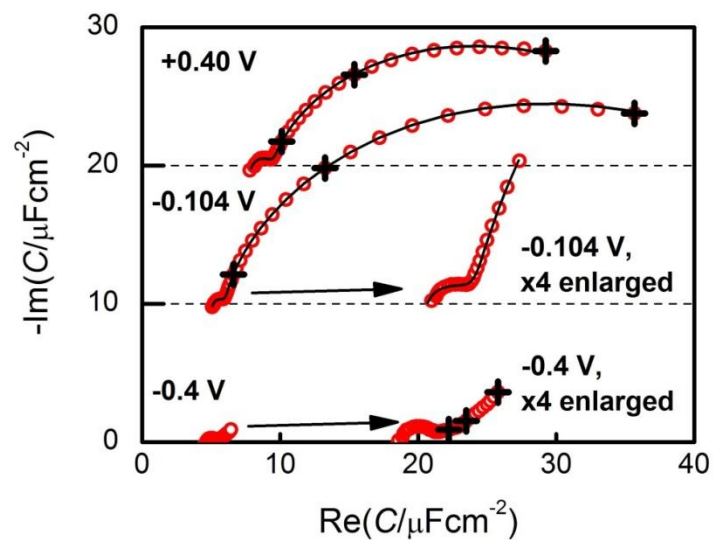
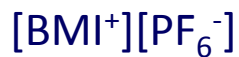


Au(100) in BMIPF₆



Stable CVs (50 mV/s), within the -0.7V and +0.5 V limits

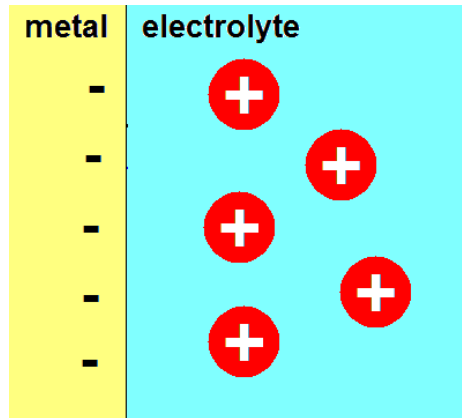




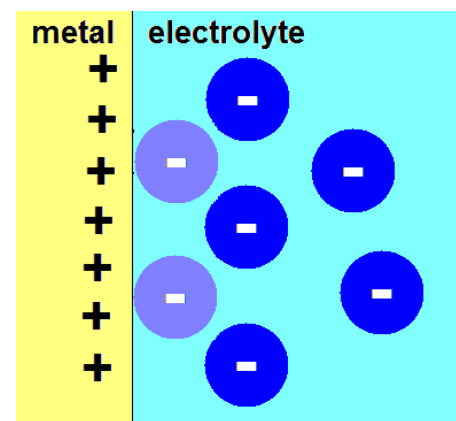
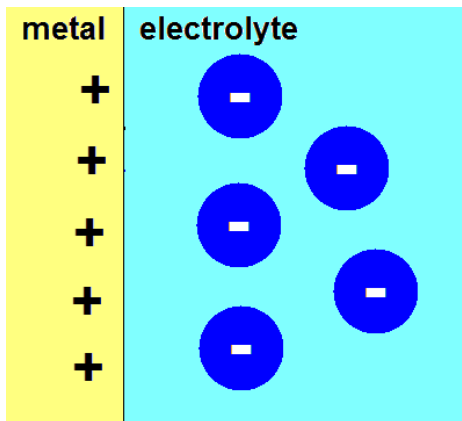
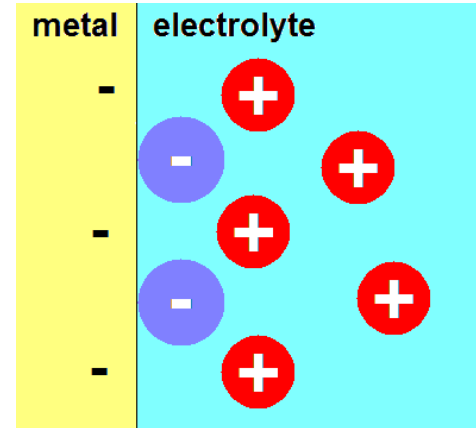
pztc

Potential of zero charge (*pzc*) definitions

1. Potential of zero
free charge, *pzfc*

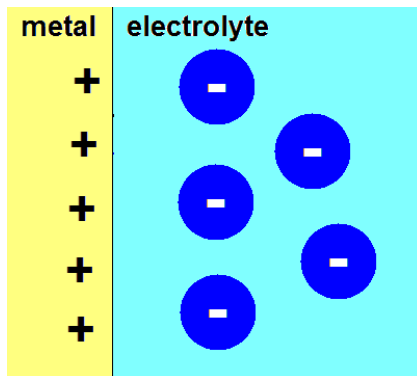
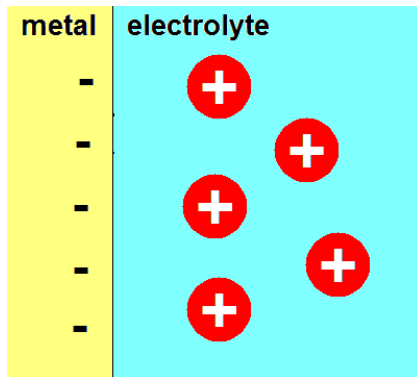


2. Potential of zero
total charge, *pztc*



pzfc is a special case of the *pztc*

Potential of zero *free* charge, *pzfc*



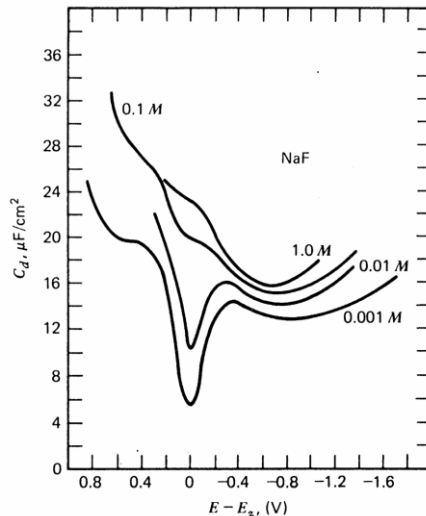
Theory:

the ions (charge carriers) attracted to / repelled from the metal; scattered by thermal motion.

Poisson-Boltzmann equation for the spatial distribution of charges. (Physical theory: no chemical interactions are assumed.)

Dilute electrolyte – metal interfaces:

Both charge carriers are free to move →
Gouy-Chapman-minimum on the $C(E)$ curve

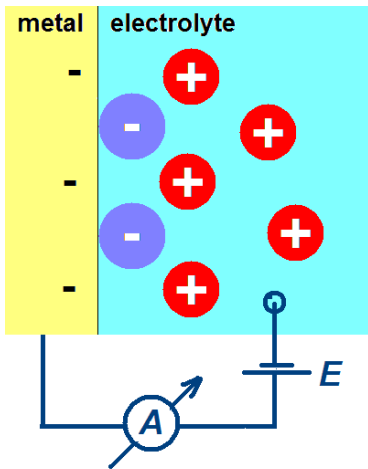
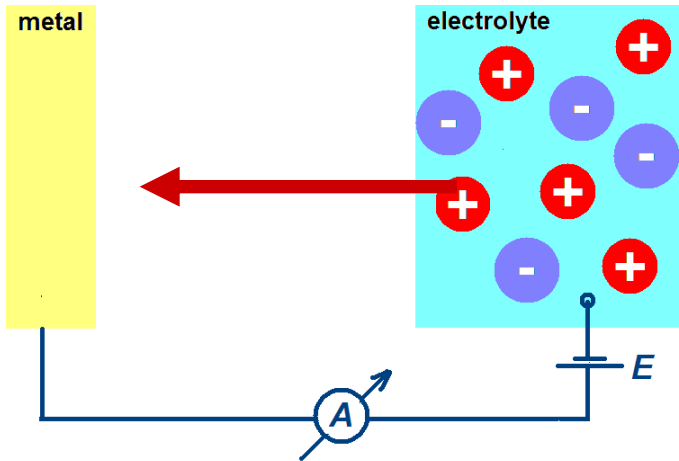


„Gouy-Chapman minimum”, Hg in NaF solution

D.C. Grahame (1947)

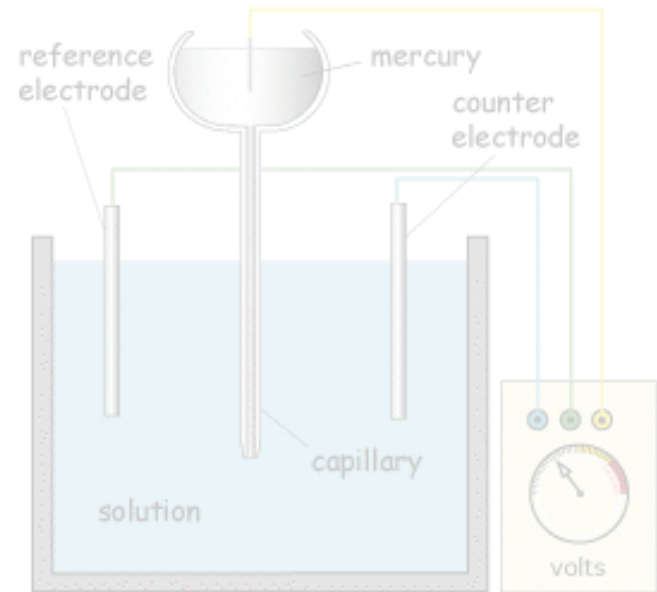
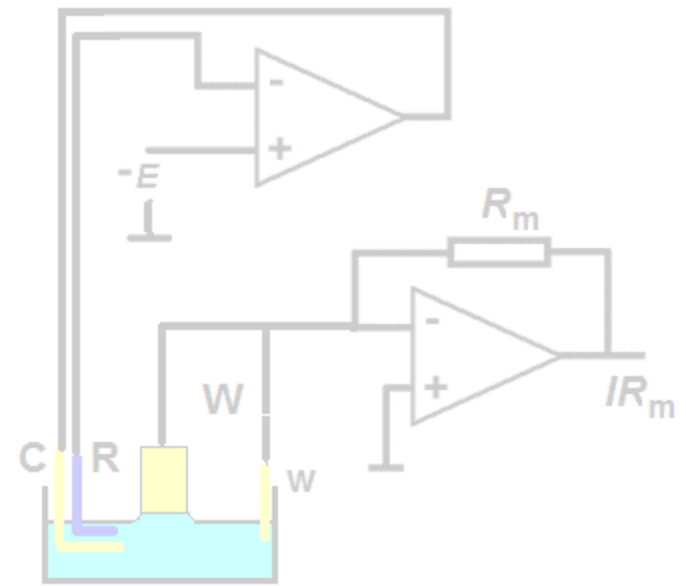
Potential of zero *total* charge, *pztc*

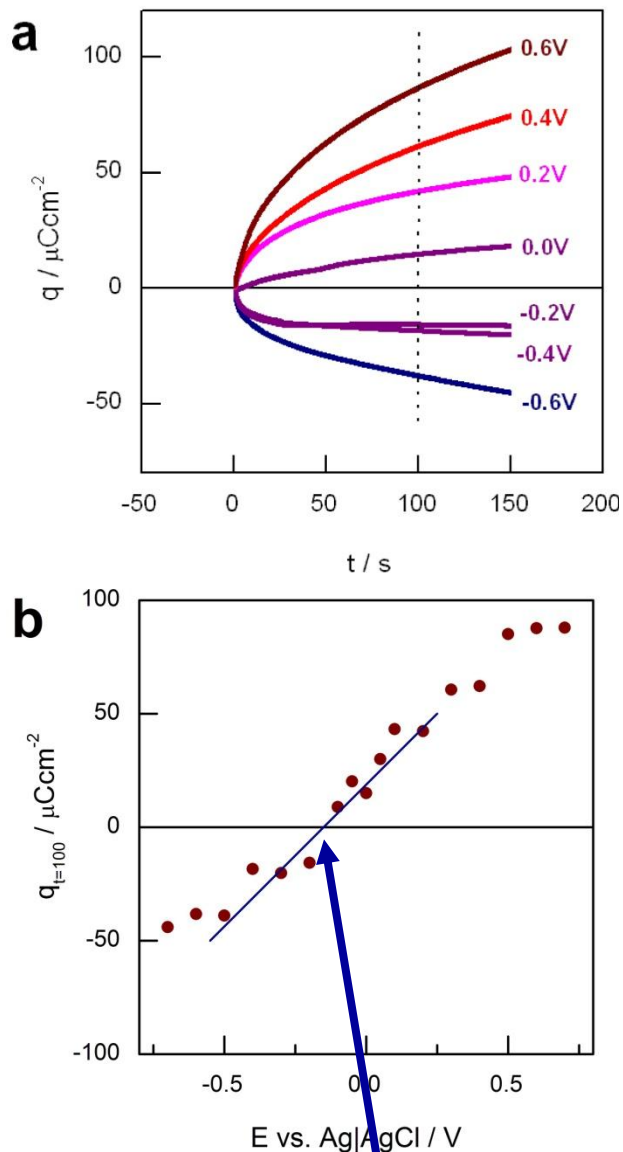
Charge needed to create the double layer:



$$q^M \equiv \int_{\text{immersion}} i(t) dt$$

$$pztc \equiv E(q^M=0)$$





The interface between Au(100) and 1-butyl-3-methyl-imidazolium-hexafluorophosphate

M. Gnahn, C. Müller, R. Répánszki,[†] T. Pajkossy^{*‡} and D. M. Kolb

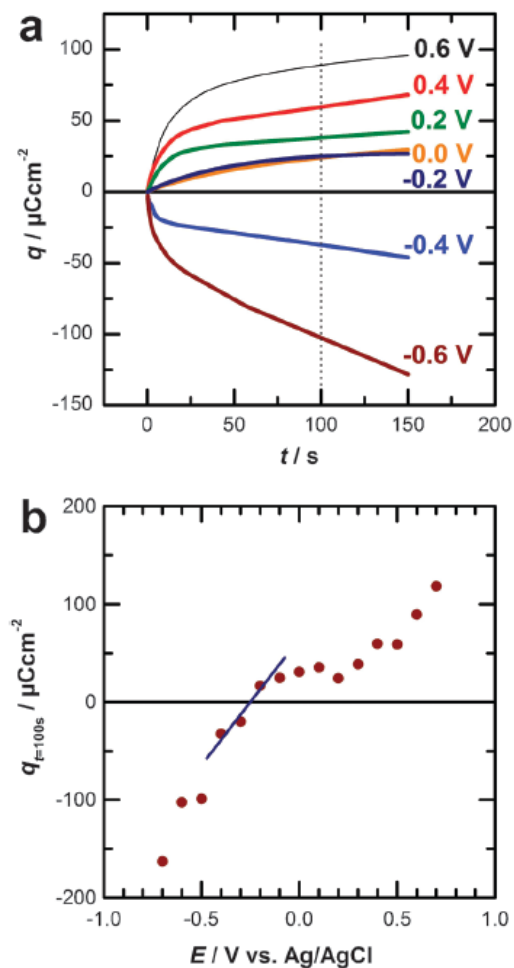
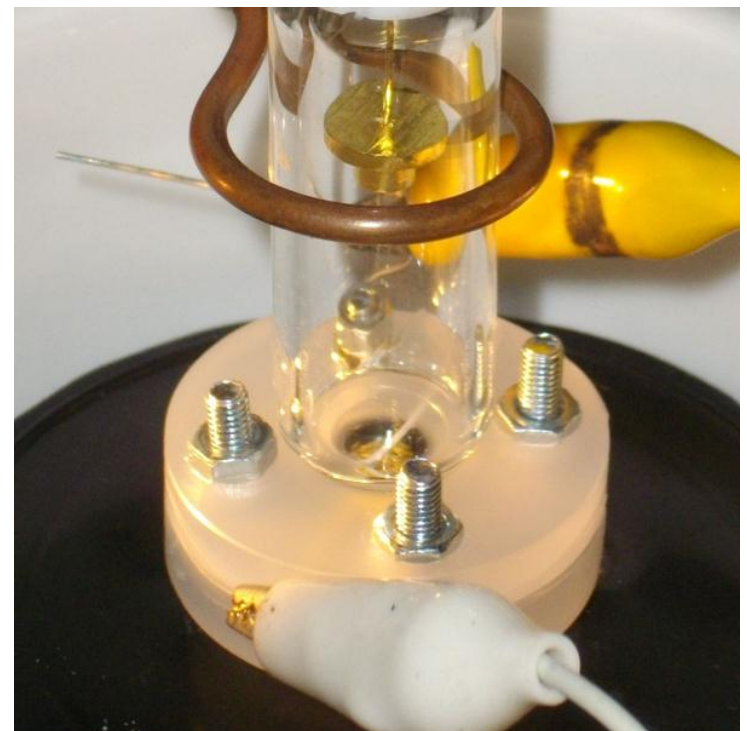
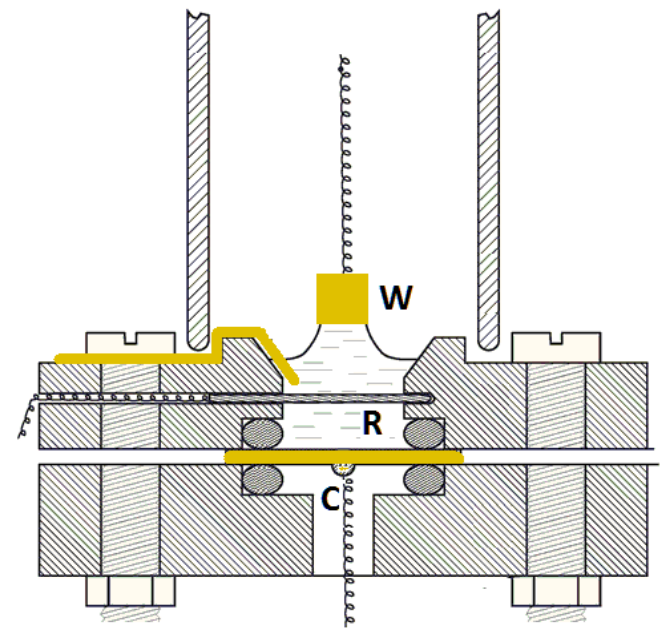
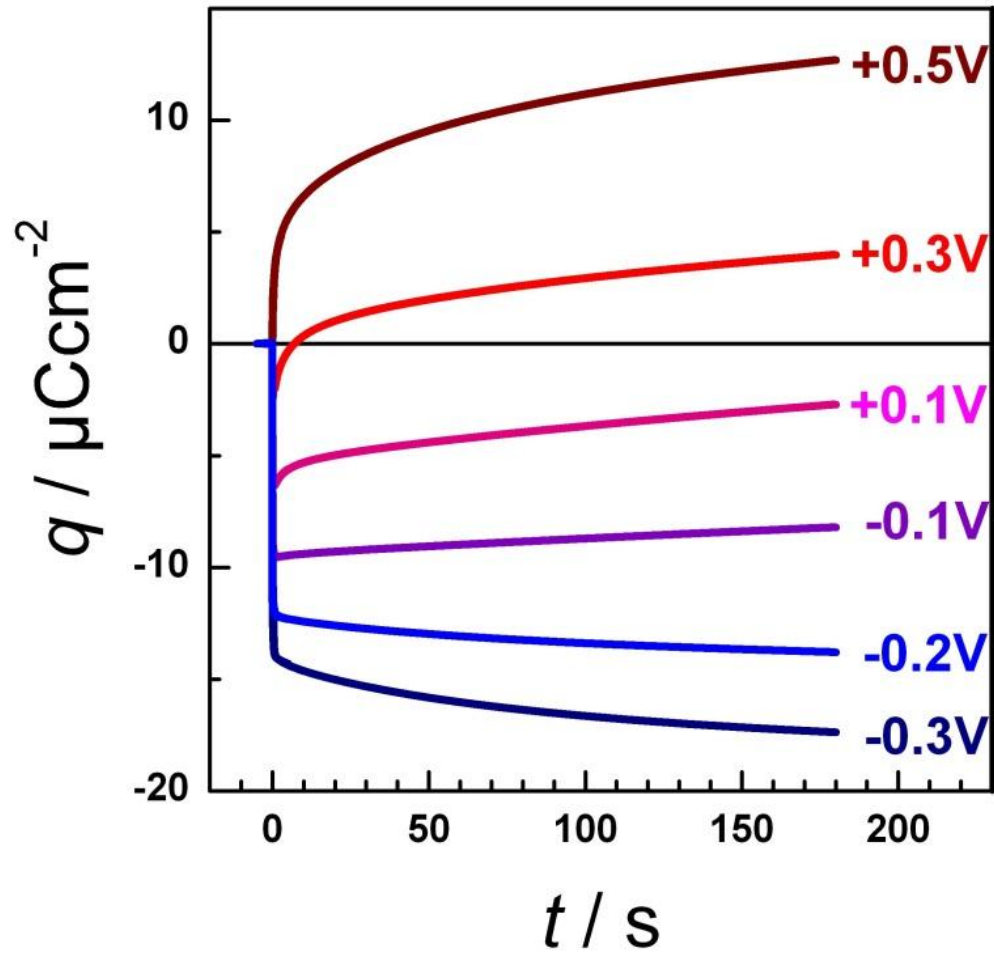


Fig. 2 (a) Integrated immersion transients at potentials indicated for Au(100) in BMIPF₆ and (b) the charge calculated for 100 s as a function of potential. The zero crossing is around -250 mV.

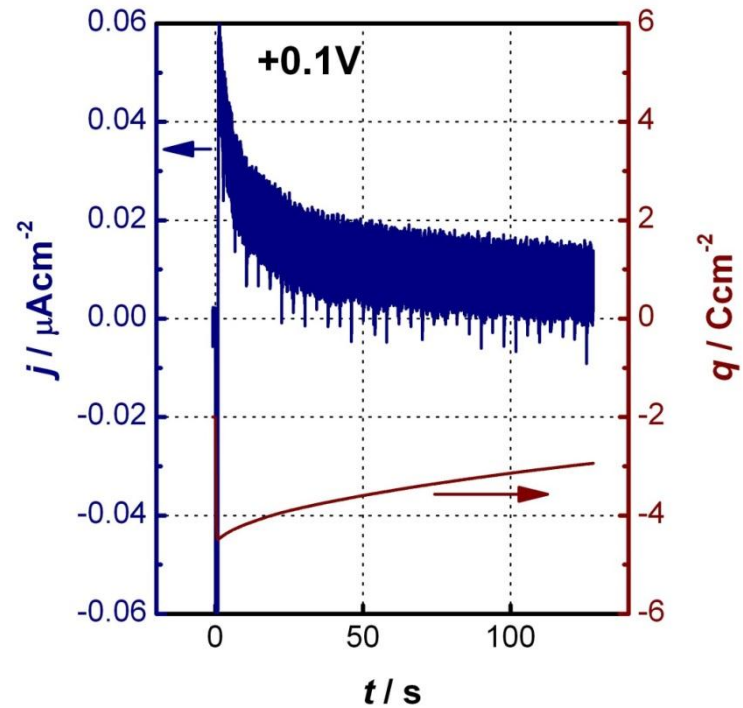
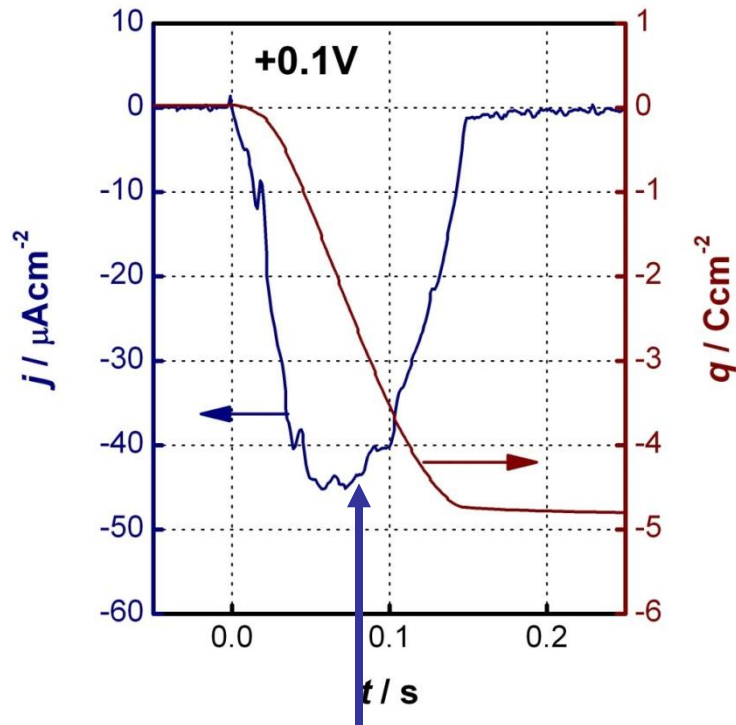




Charge vs time ($-300\text{mV} < E < 600\text{mV}$)

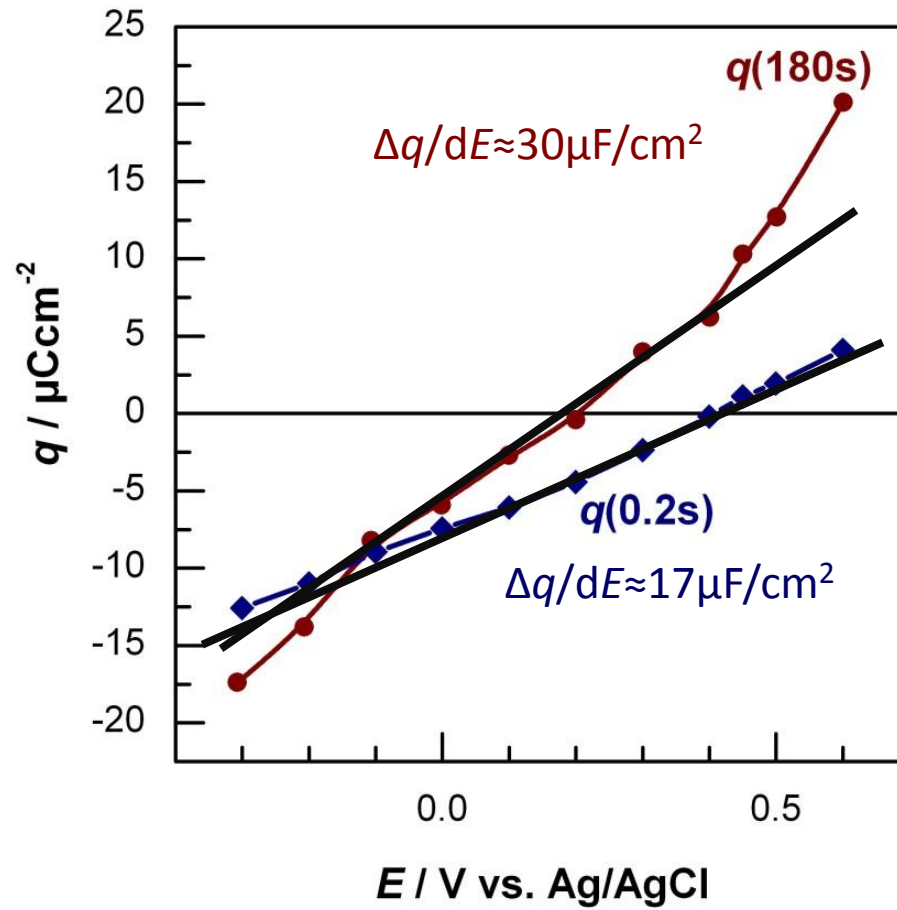


Current and charge vs time @+0.1 V, short and long times



Instantaneous charging
(with the wetting)

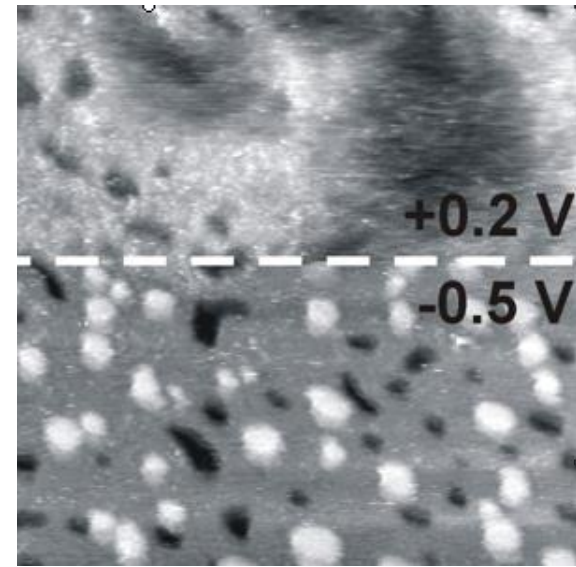
Immersion charge vs potential at long and short times



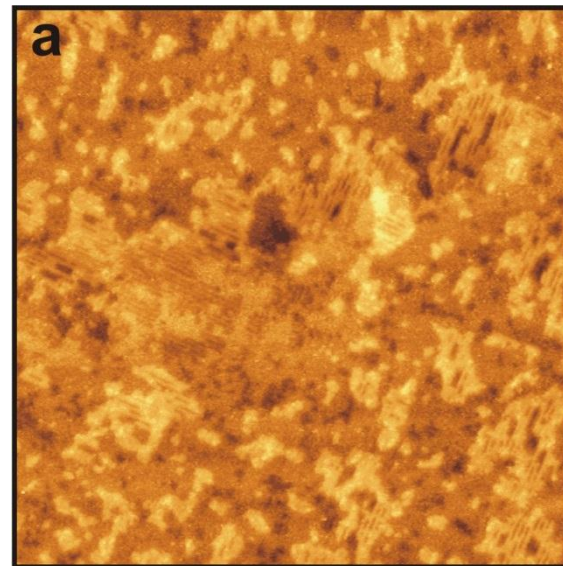
Interpretation

pztc, additional findings: *in-situ* STM images

1. Au(111)|BMIPF₆ (100x100 nm)
at +0.2V and -0.5V (M. Gnahn, 2008)

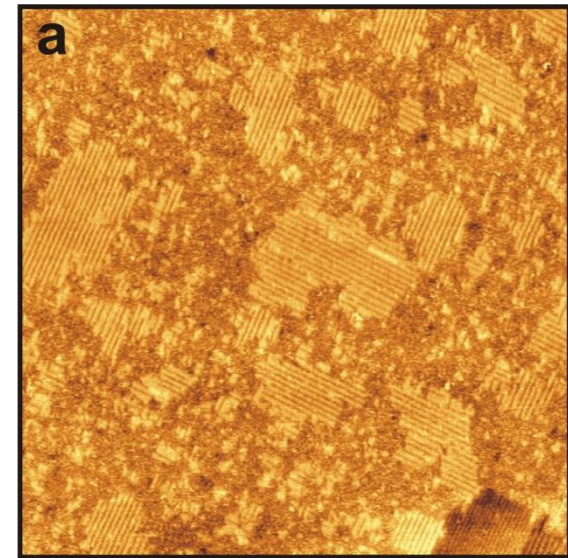


2. Au(100)|BMITf₂N (250x250 nm)
at +0.043V and -0.2V (C. Müller, 2014)



250 nm x 250 nm

$E_{\text{Ag/AgCl}} = -0.2 \text{ V}$



250 nm x 250 nm

$E_{\text{Ag/AgCl}} = +0.043 \text{ V}$

The change is reversible (albeit very slow) → the tip senses the surface through different interfacial layers.

discussion



Double layer in ionic liquids: The nature of the camel shape of capacitance

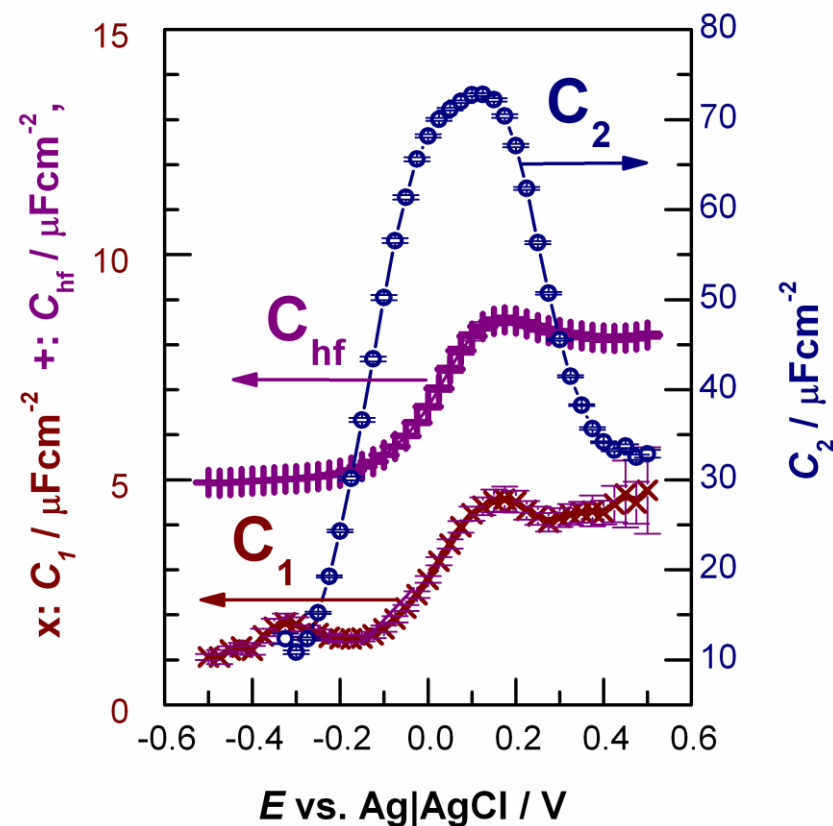
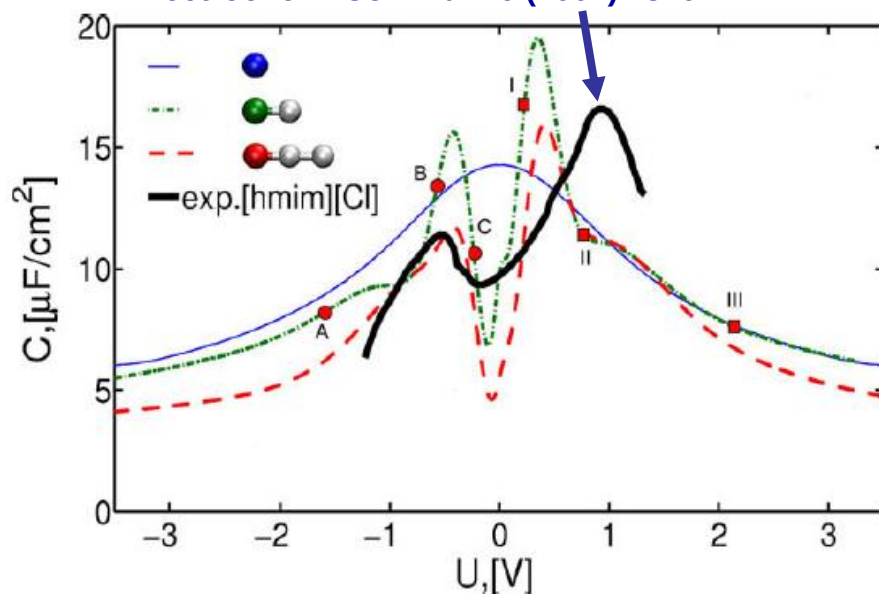
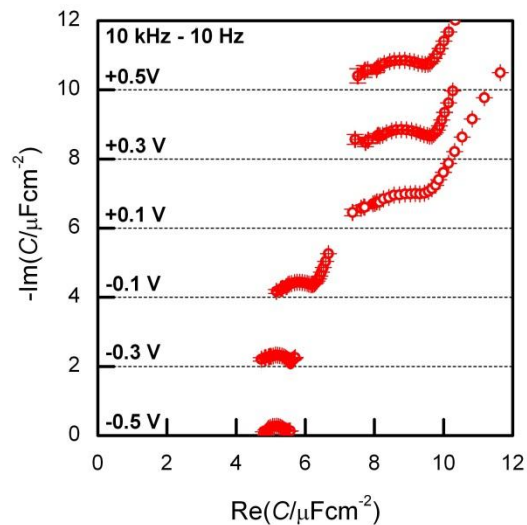
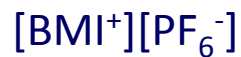
M.V. Fedorov^{a,*}, N. Georgi^a, A.A. Kornyshev^{b,*}^aMax-Planck Institute for Mathematics in the Sciences, Inselstrasse 22, D 04103 Leipzig, Germany^bDepartment of Chemistry, Imperial College London, SW7 2AZ London, UKM.T. Alam, M.M. Islam, T. Okajima, T. Ohsaka,
Electrochem. Commun. 9 (2007) 2370.

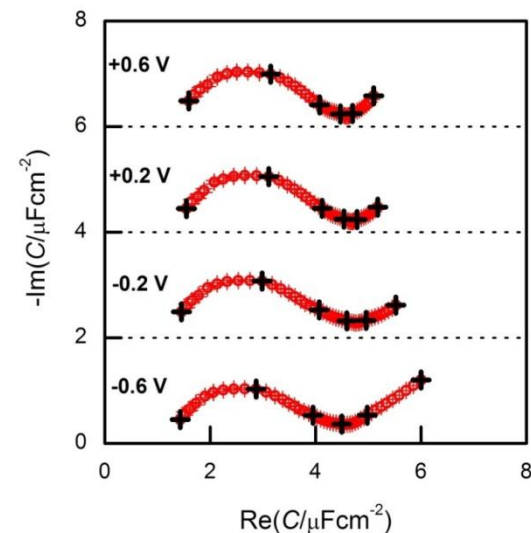
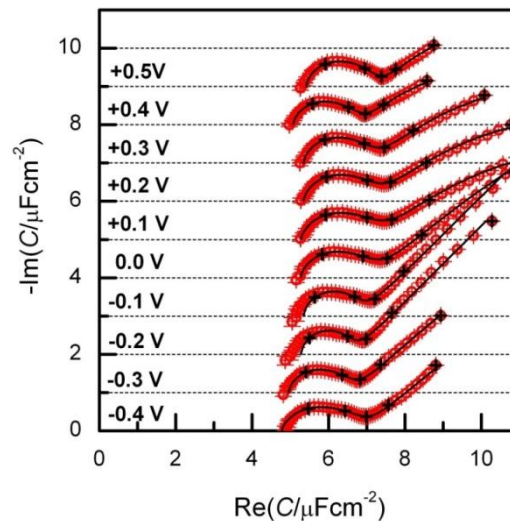
Fig. 1. Differential capacitance obtained from simulations. The maxima are located



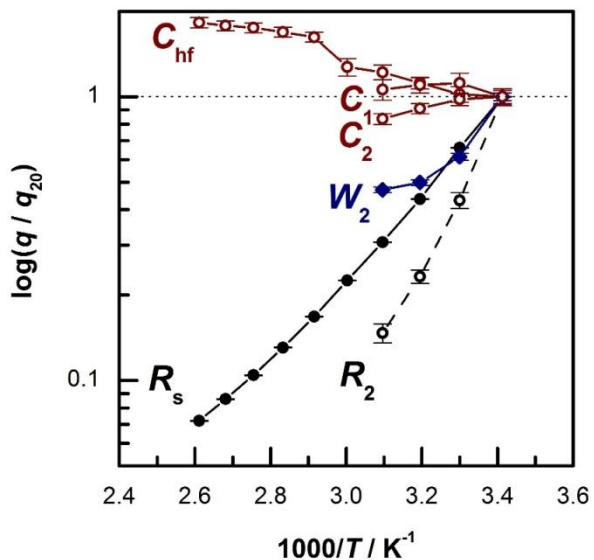
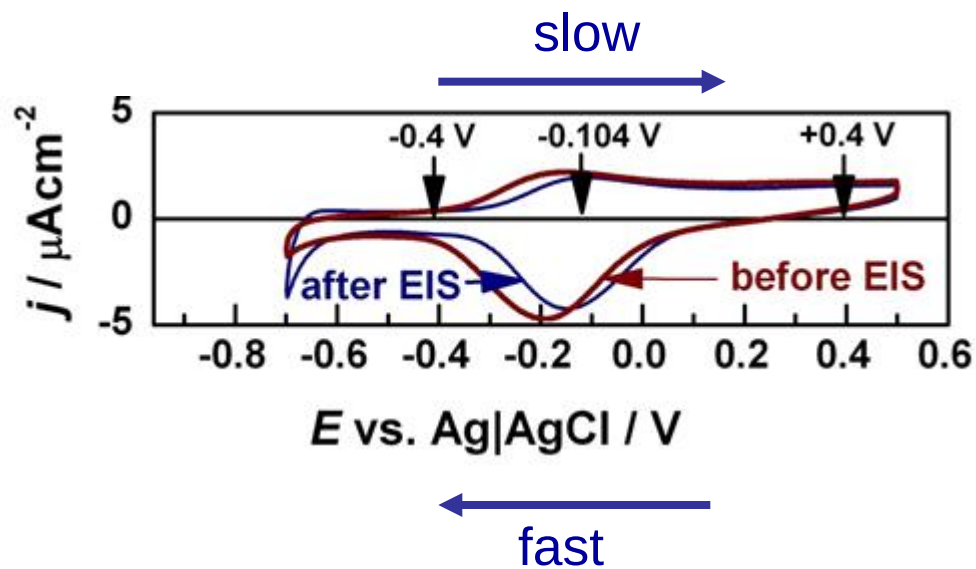
C_{hf} for $[\text{BMI}^+]$:

$5 \mu\text{F}/\text{cm}^2$

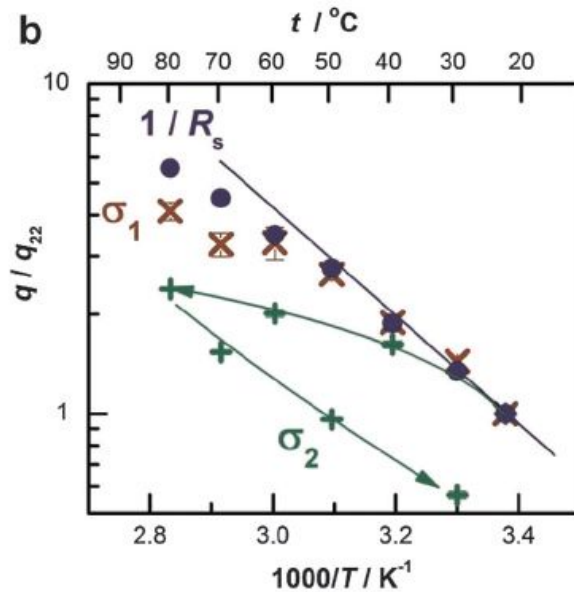
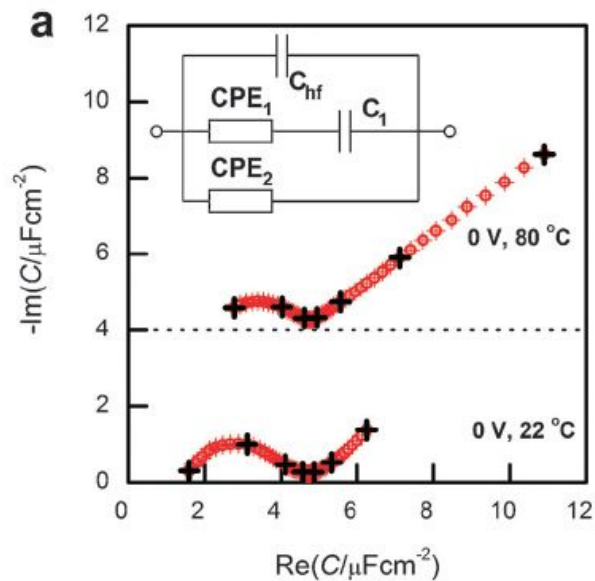
C_{hf} for $[\text{N}_{11}\text{N}_{22}\text{N}_{44}\text{Gu}^+\text{BMI}^+]$: $1 \mu\text{F}/\text{cm}^2$



Kinetics, $[\text{BMI}^+][\text{PF}_6^-]$



$[\text{N}_{11}\text{N}_{22}\text{N}_{44}\text{Gu}^+][\text{Tf}_2\text{N}^-]$



Summary:

Impedance (and pztc and in-situ STM) experiments have been done on Au|ionic liquid electrodes.

The main statement:

The double layer formation and rearrangements are slow processes (much slower than eg. in aqueous systems).

Open issues:

1. Impedance: what is the physical meaning of the two arcs on the capacitance spectra (in particular of the R-W elements in the equivalent circuit)?
Is it possible to assign the arcs to the ions?



2. Immersion: what are the two charging processes (the fast and the slow)?

Help is needed in theorizing.

Acknowledgments:

Financing: DFG, DAAD, HAS, OTKA, MÖB

Cooperation, friendship, hospitality: †Dieter Kolb and colleagues

Organizers for the invitation