Barrier properties of surface layers at the electrode/electrolyte interface: challenges for alternative metal-ion batteries development

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19.09.2017

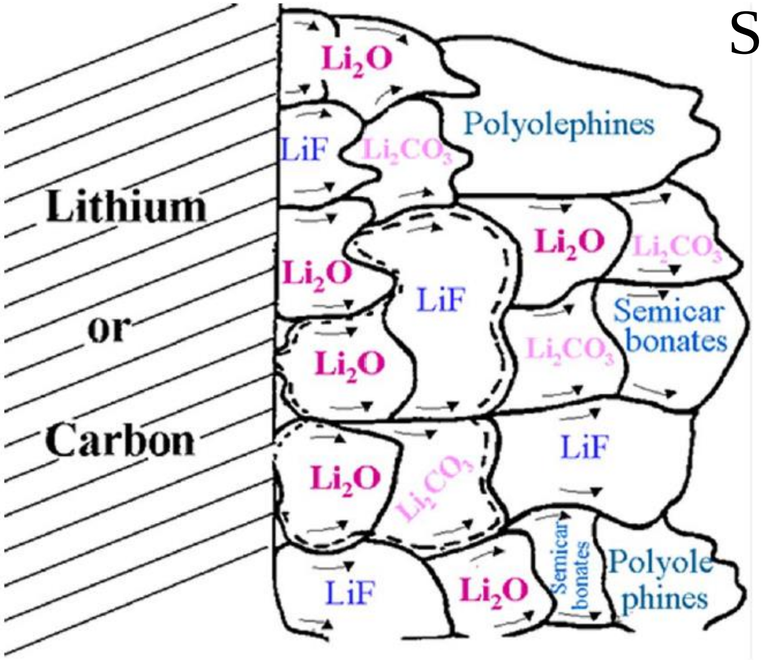
1. Introduction
2. Electrochemistry of surface layers
3. CEI effects in superconcentrated electrolytes
4. CEI effects in K^+ intercalation kinetics

I. Thick SEI layers – we think we know what they are made of

SEI – solid electrolyte with high electronic resistivity (E. Peled)

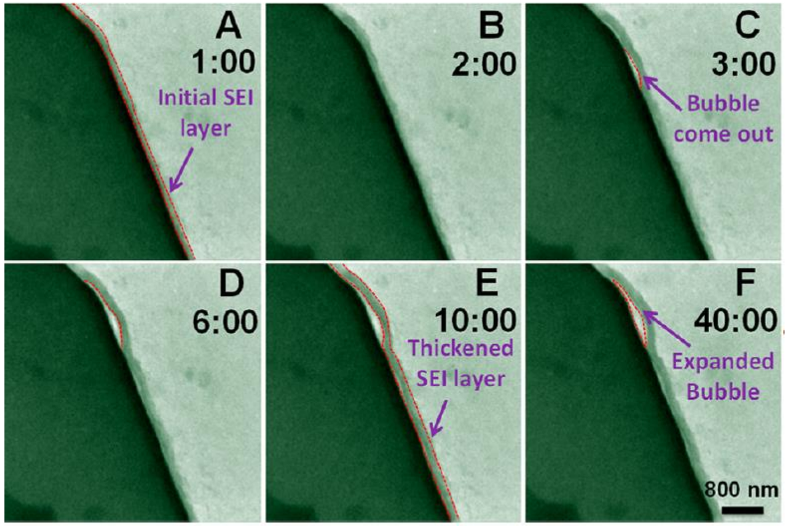
- high electrical resistance and high cation selectivity and permeability
- thickness close to a few nanometers
- tolerance to expansion and contraction
- insolubility in the electrolyte
- high stability

The barrier of ca. 20 Å blocks electronic tunneling



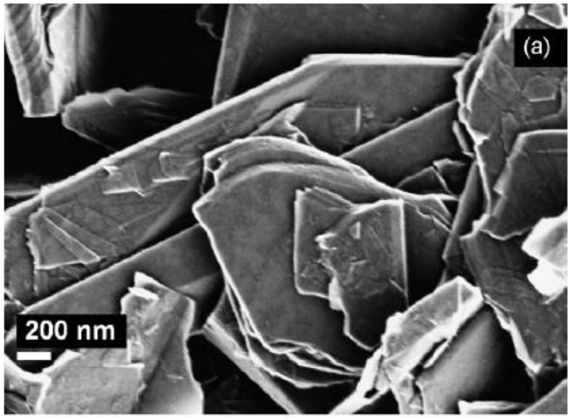
E. Peled et al., *J. Electrochem. Soc.*, 164 (2017) A1703

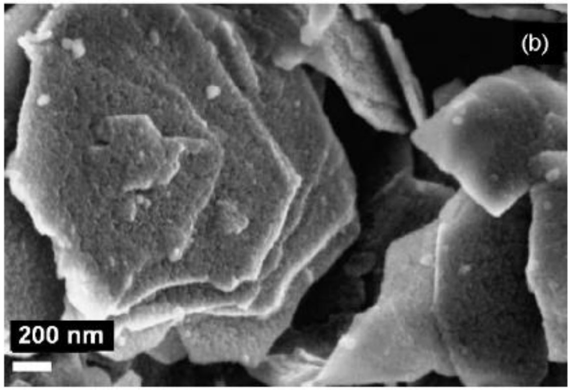
SEI at lithiated Au in comm. electrolyte



Z. Zeng et al., *Nano Lett.* 2014, 14, 1745−1750

Pristine graphite

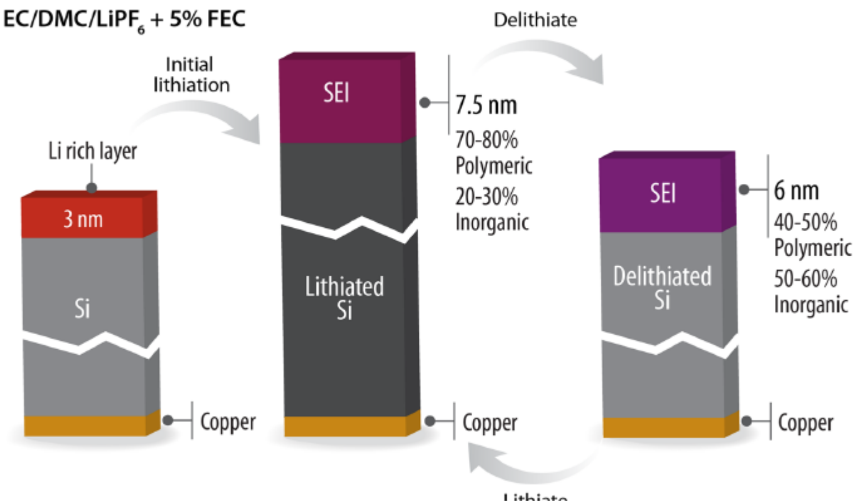


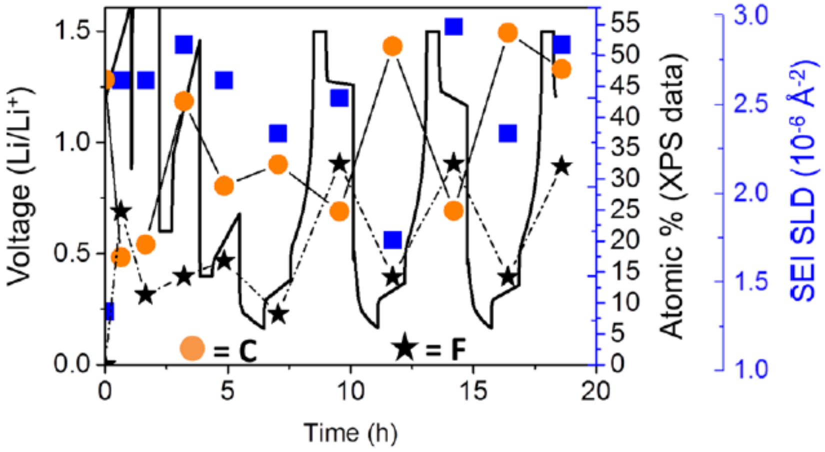


Graphite after cycling in
1 M $LiPF_6$ in EC:DEC

P. Verma et al. *Electrochim. Acta* 55 (2010) 6332–6341

"Breathing" SEI layer at silicon anode

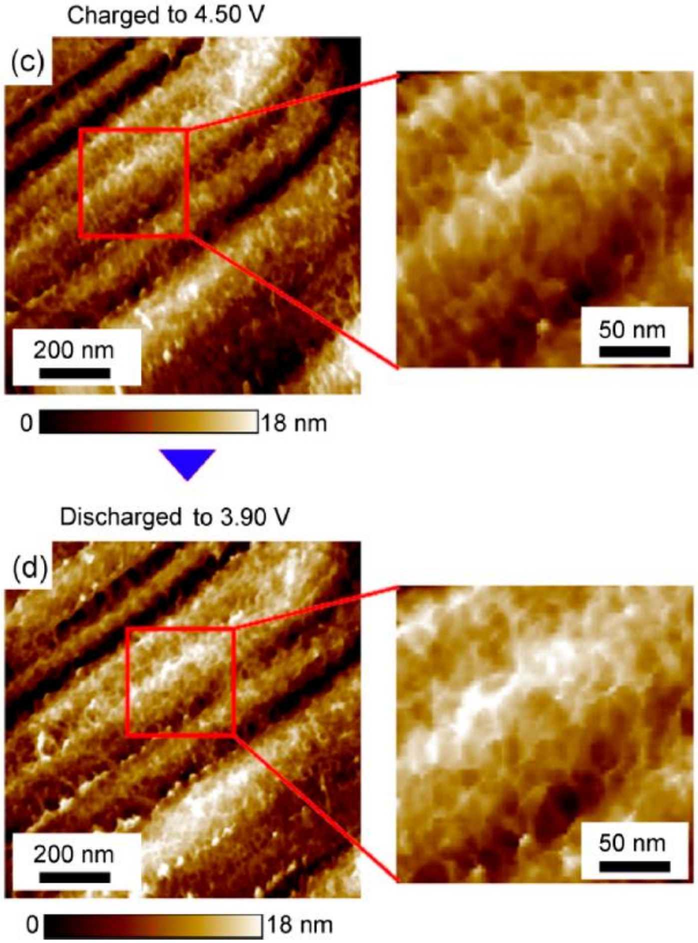




G. Veith et al. *Scientific Reports* **7 (2017)** 6326

CEI layers – so thin that some people don’t believe they exist

CEI formation on the edge planes of $LiCoO_2$



W. Lu et al. *ACS Appl. Mater. Interfaces* 9 (2017) 19313

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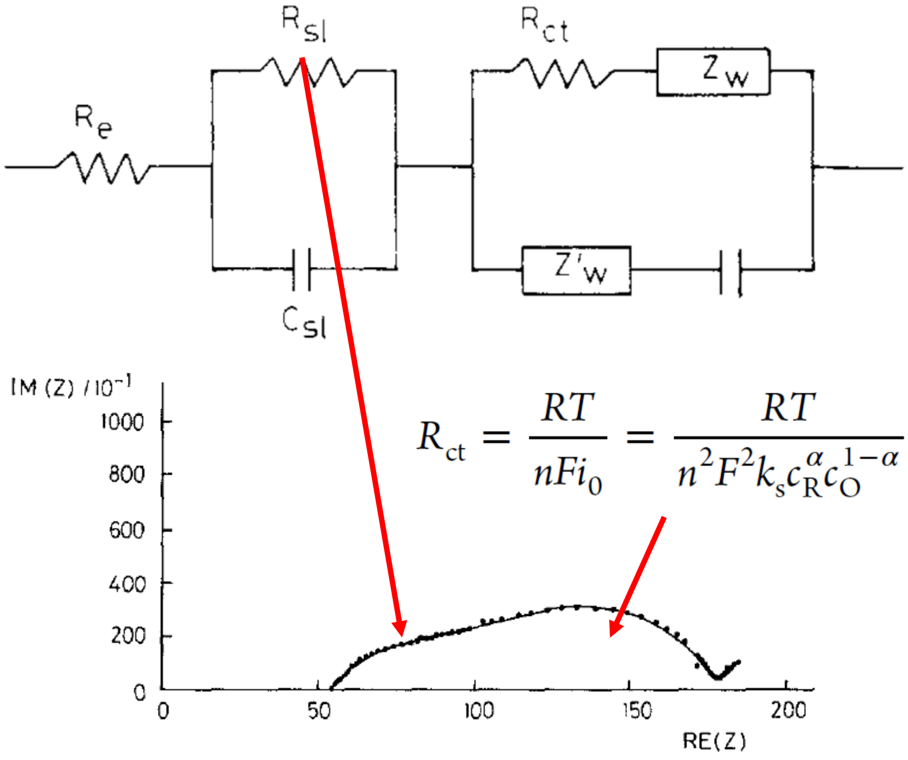
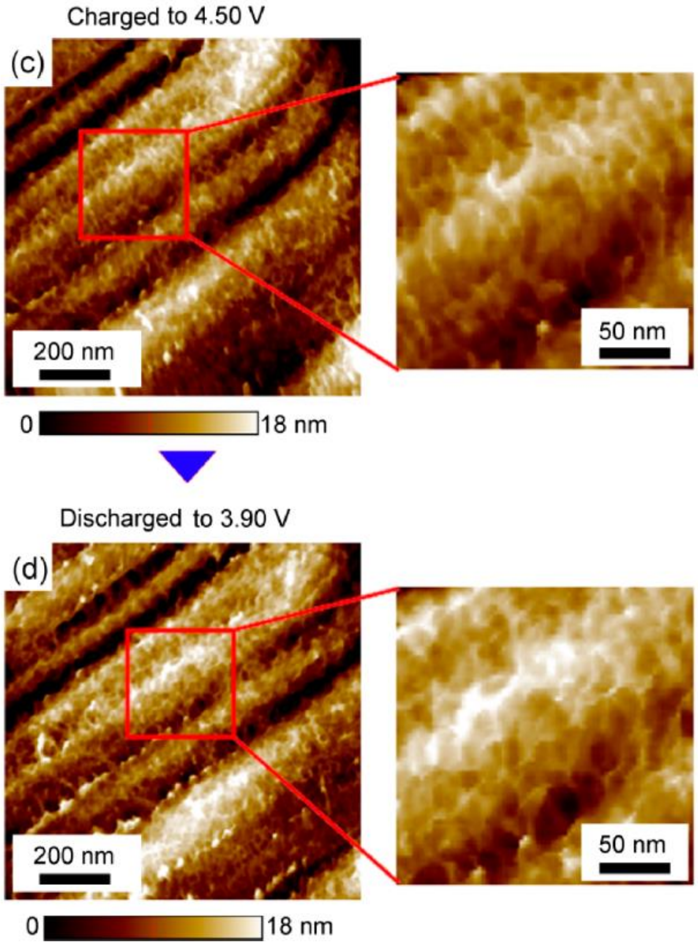
Equivalent circuit to model surface layers



$$R_{ct} = \frac{RT}{nFi_0} = \frac{RT}{n^2F^2k_sc_R^{\alpha}c_O^{1-\alpha}}$$

M. Thomas et al., *J. Electrochem. Soc.* 132 (1985) 1521

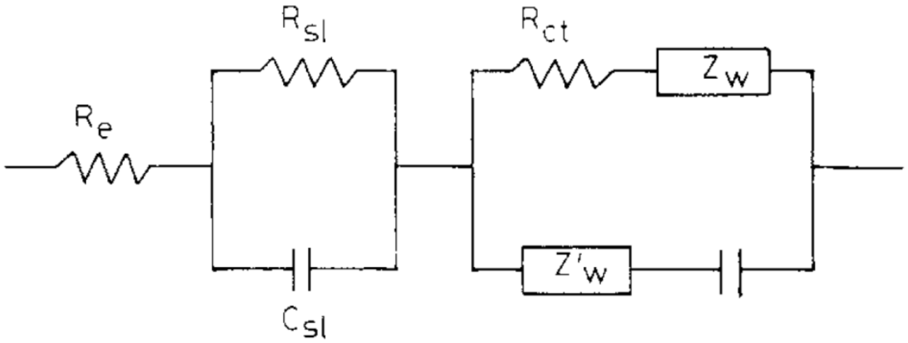


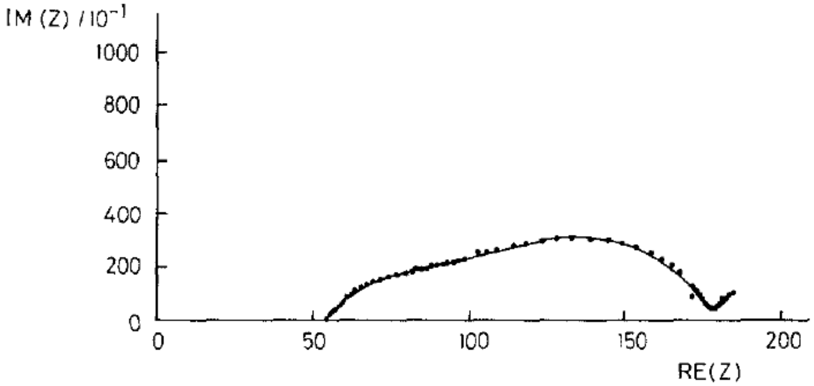
W. Lu et al. *ACS Appl. Mater. Interfaces* 9 (2017) 19313

Thin CEI layers – we know little

CEI formation on the edge planes of $LiCoO_2$

Equivalent circuit to model surface layers





M. Thomas et al., *J. Electrochem. Soc.* 132 (1985) 1521

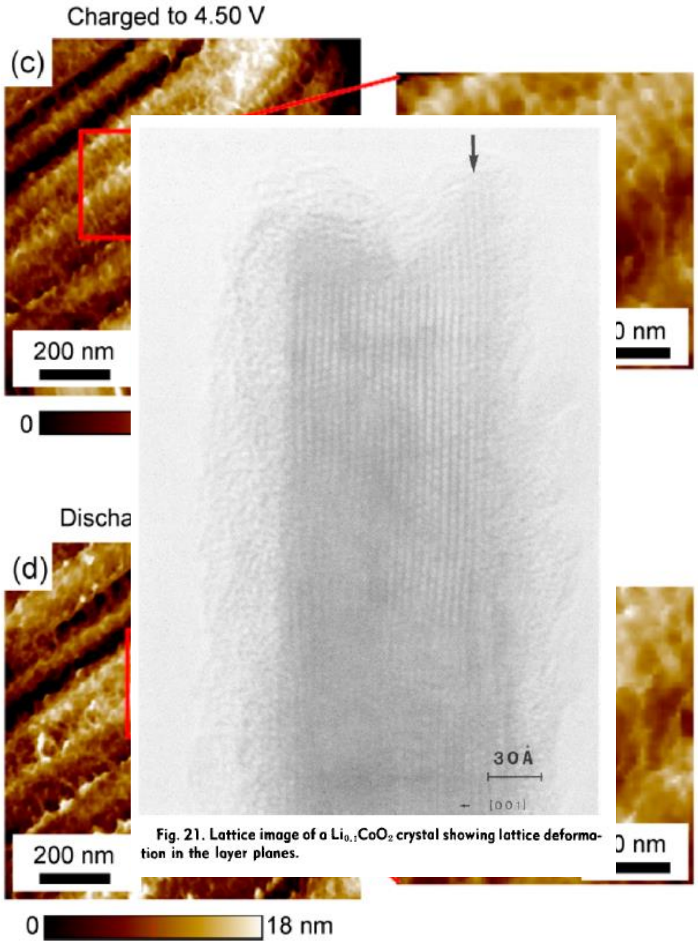
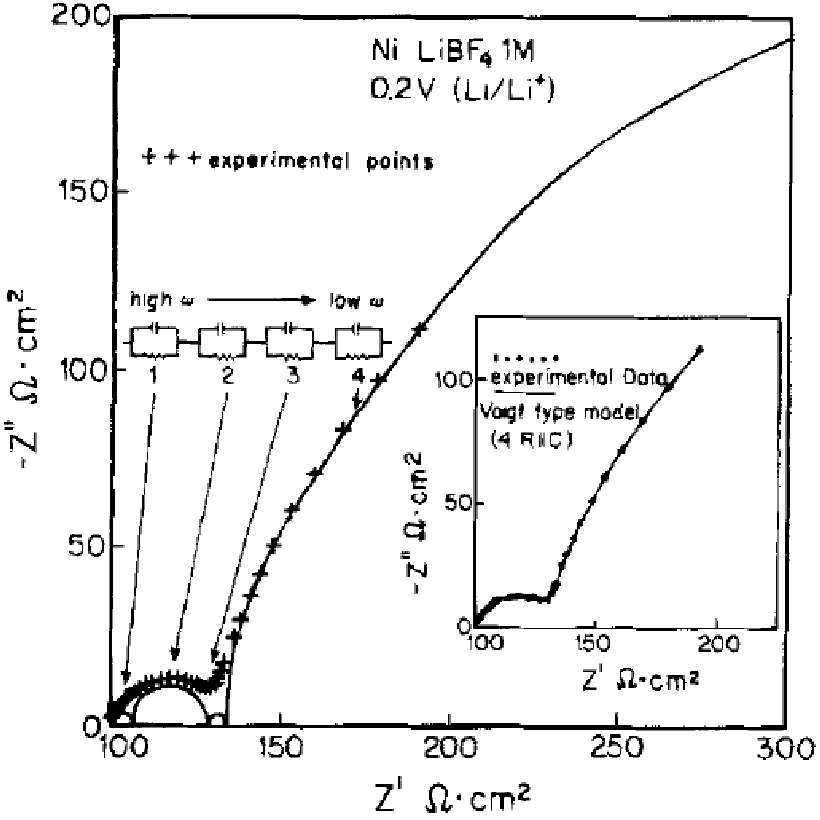
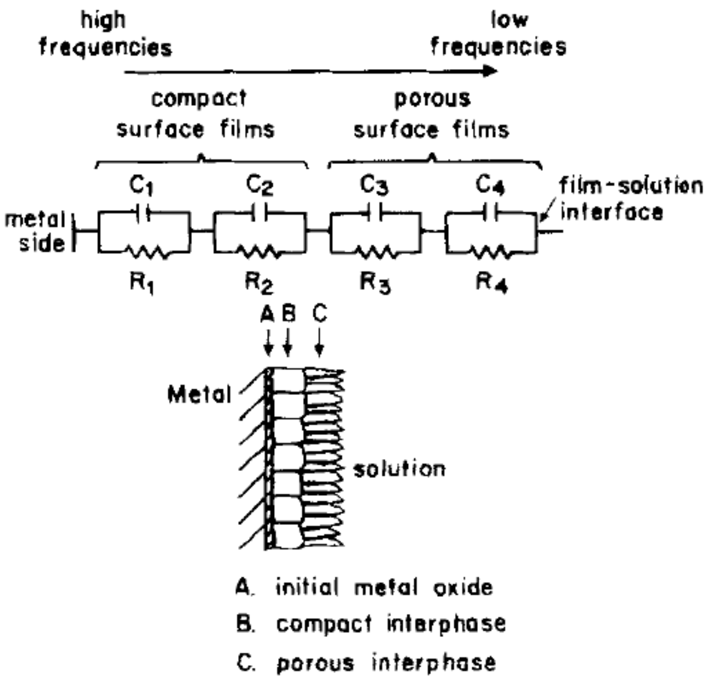


Fig. 21. Lattice image of a $Li_{0.1}CoO_2$ crystal showing lattice deformation in the layer planes.

W. Lu et al. *ACS Appl. Mater. Interfaces* 9 (2017) 19313

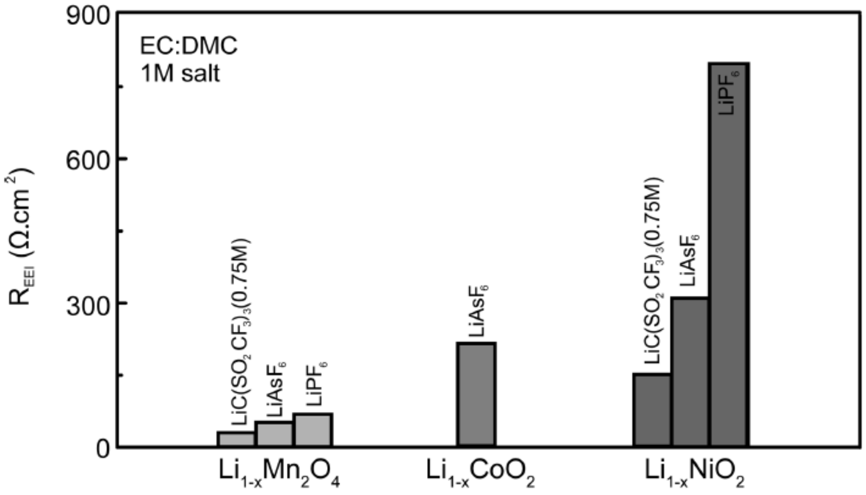


Scheme 1



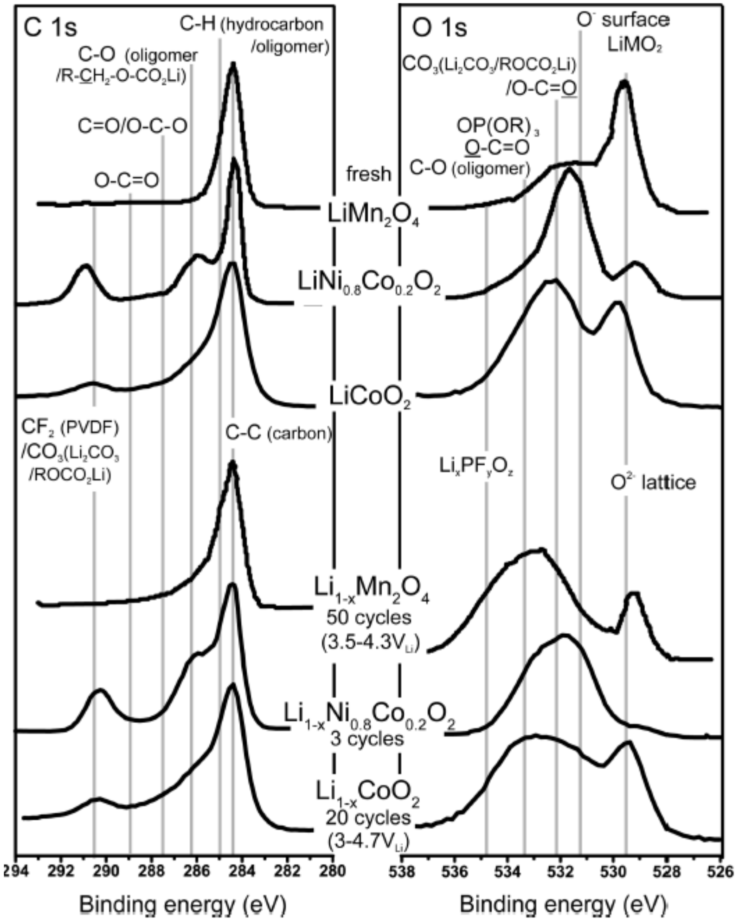
D. Aurbach et al. *J. Electrochem. Soc.* 141 (1994) 1808

Interface resistance is highly dependent on the salt and the TM



Similar species (as in SEI) can be detected: carbonates, semicarbonates $ROCO_2Li$, alkoxides ROLi, LiF, organophosphates $Li_xPF_yO_z$, PEO, polyethers, etc

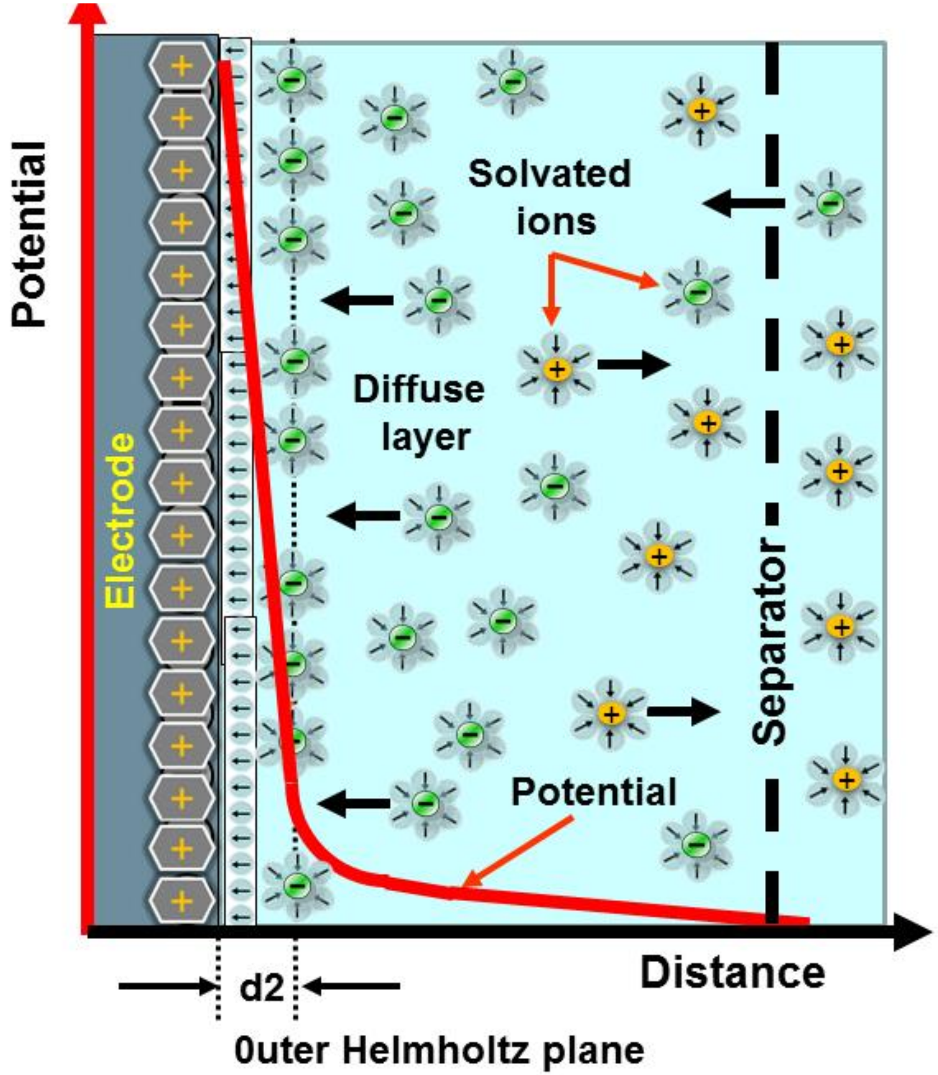
D. Aurbach et al., *J. Electrochem. Soc.* 147 (2000) 1322
S. Verdier et al., *J. Electrochem. Soc.* 154 (2007) A1088



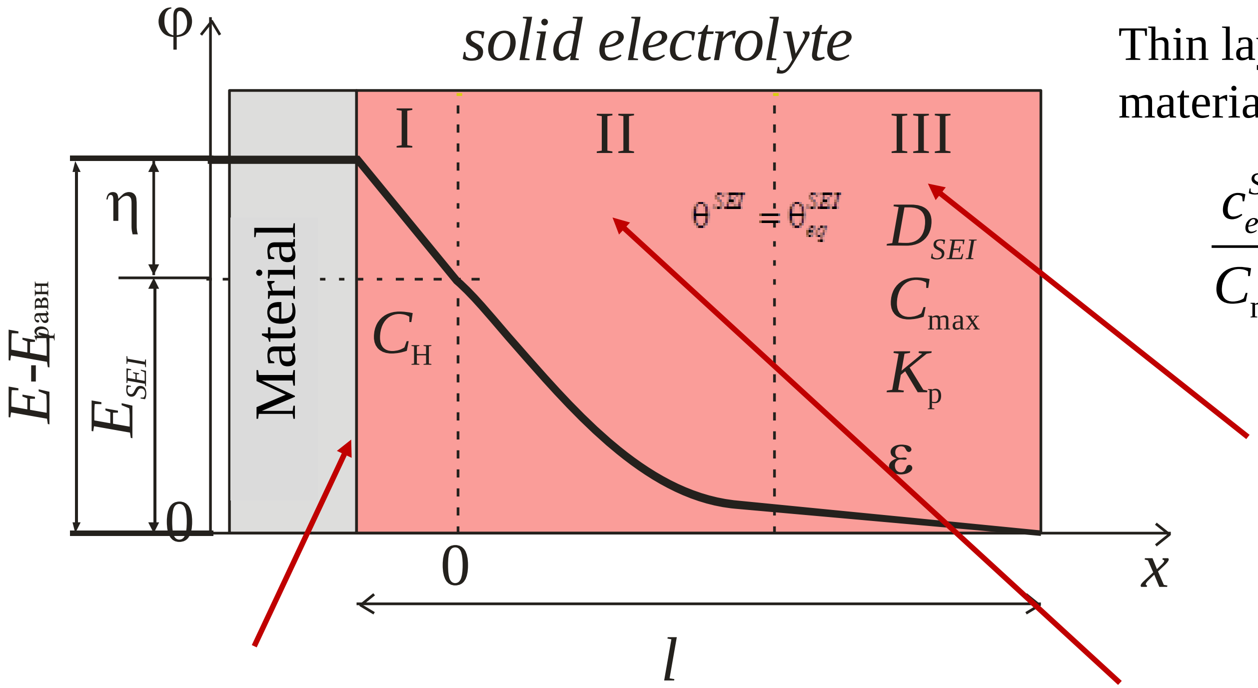
In situ neutron reflectometry,
In situ XPS and XAS:
CEI is few nm in thickness
(carbonates, oxides, fluorides)

Classical double layer

$$i = nFAk^{s}\left[c_{Ox}^{S}\exp\frac{-\alpha nF\eta}{RT} - c_{\mathrm{Red}}^{S}\exp\frac{(1-\alpha)nF\eta}{RT}\right]$$



The simplest surface layer model



Thin layer of solid electrolyte at the material surface

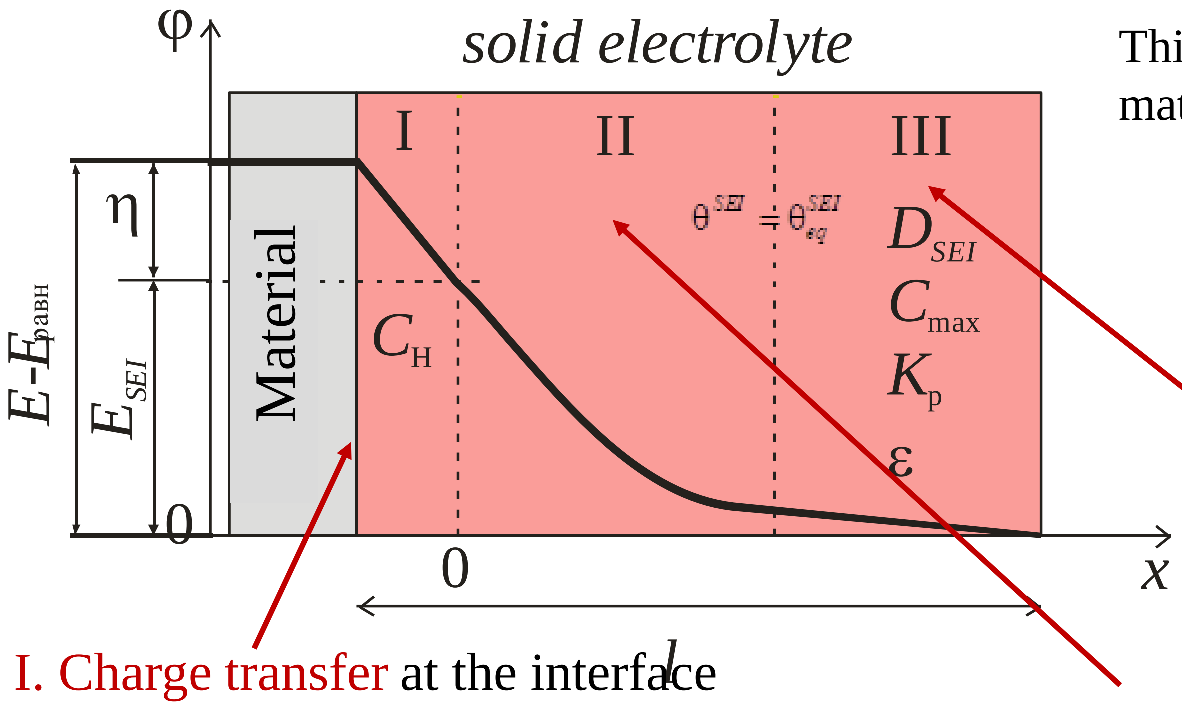
$$\frac{c^{SEI}_{eq}}{C_{max}} = \theta^{SEI}_{eq} = \frac{K_p}{1+K_p}$$

III. Bulk solution
Migration of Li^+ ions;
equilibrium concentration

I. Charge transfer at the interface material/“compact part” of the double layer

II. “Diffuse part” of the double layer

The simplest surface layer model



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Migration of Li$^+$ ions;
equilibrium concentration

I. Charge transfer at the interface material/“compact part” of the double layer

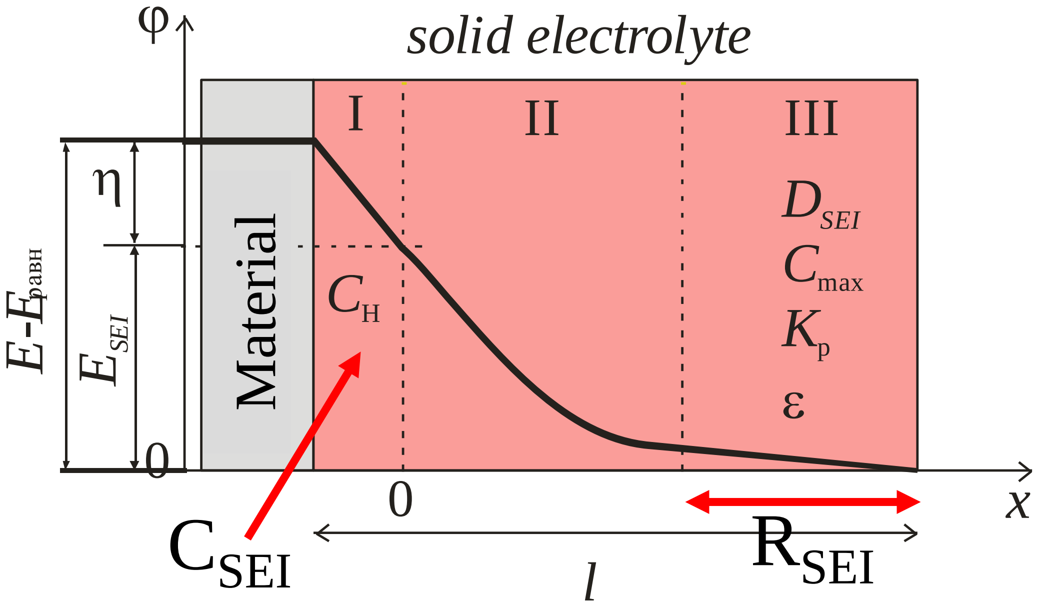
II. “Diffuse part” of the double layer

Without CEI

$$I(E) = SF\cdot 10^6\cdot\frac{\rho\cdot n_{\mathrm{Li}}}{M_r}\cdot k_s\cdot\left\{\theta\cdot\exp\left[\frac{(1-\alpha)F(E-E_0(\theta))}{RT}\right]-(1-\theta)\cdot\exp\left[-\frac{\alpha F(E-E_0(\theta))}{RT}\right]\right\}$$

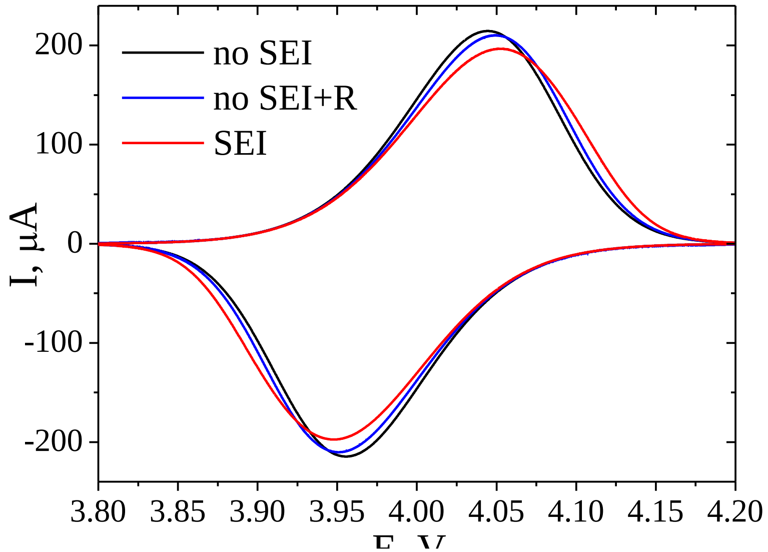
With CEI

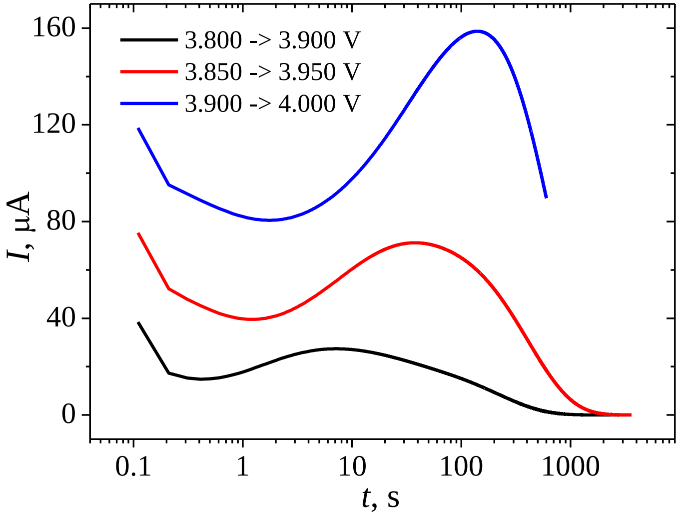
$$j_{\mathrm{int}} = \frac{I(\eta)}{SF\cdot 10^6} = \frac{\rho\cdot n_{\mathrm{Li}}}{M_r}\cdot C_{\max}k_s^{SEI}\cdot\left\{\theta(1-\theta^{SEI})\cdot\exp\left[\frac{(1-\alpha)F\eta}{RT}\right]-(1-\theta)\theta^{SEI}\cdot\exp\left[-\frac{\alpha F\eta}{RT}\right]\right\}$$

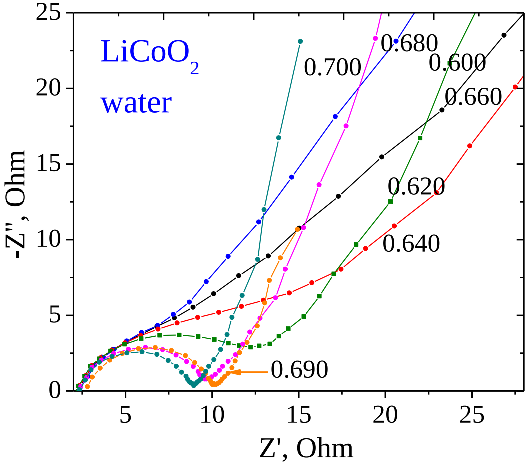


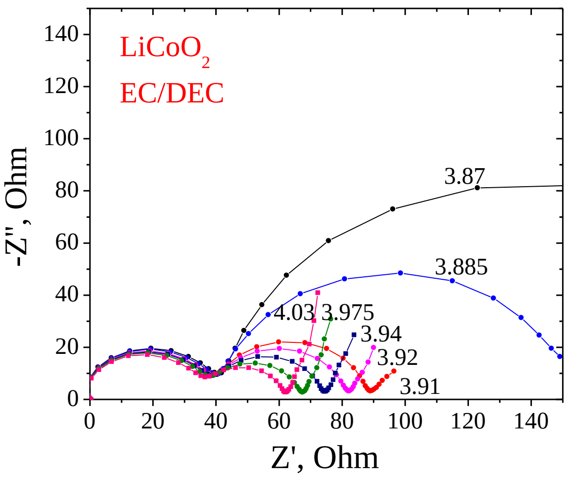
- ❖ The charge transfer is now controlled not only by **the concentration of A^+ and vacancies in the material** but also **by the concentrations in SEI layer**

- Weak effect on small step current transients (short times) (correct *D* estimation)
- Large effect on current transients





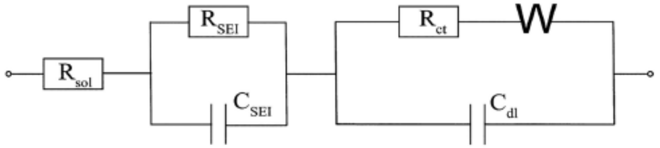




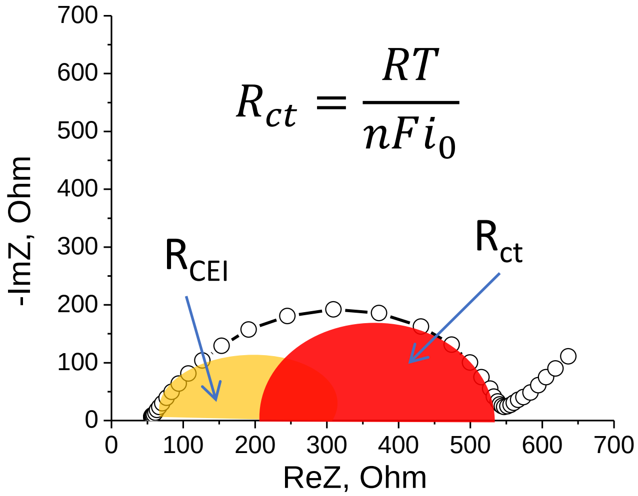
- Extra low loadings
- Three-electrode cell
- Large electrolyte V

Clearly, intercalation mechanism is not that simple

$$R_{ct} = \frac{RT}{nFi_0} = \frac{RT}{n^2F^2k_s c_R^{\alpha} c_O^{1-\alpha}}$$



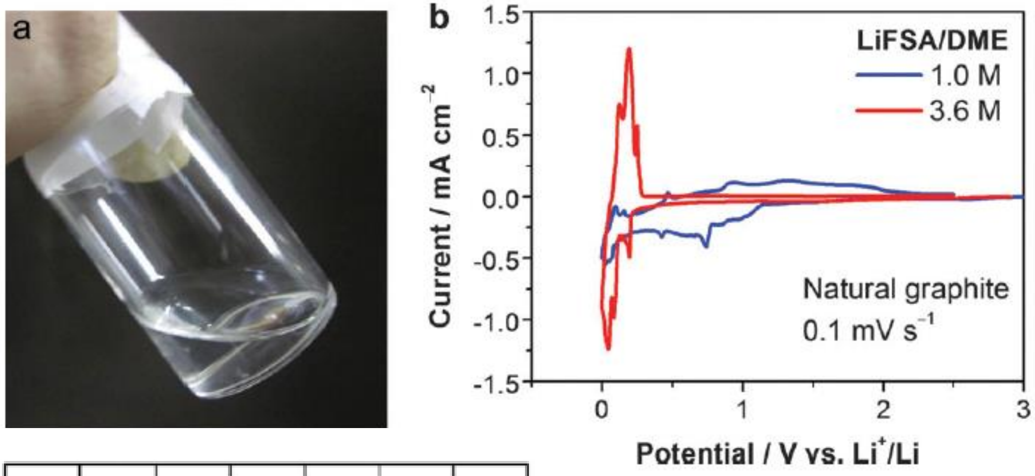
The resolution of the semicircles depends on ratio of the time constants of the two contours



$$R_{ct} = \frac{RT}{nFi_0}$$

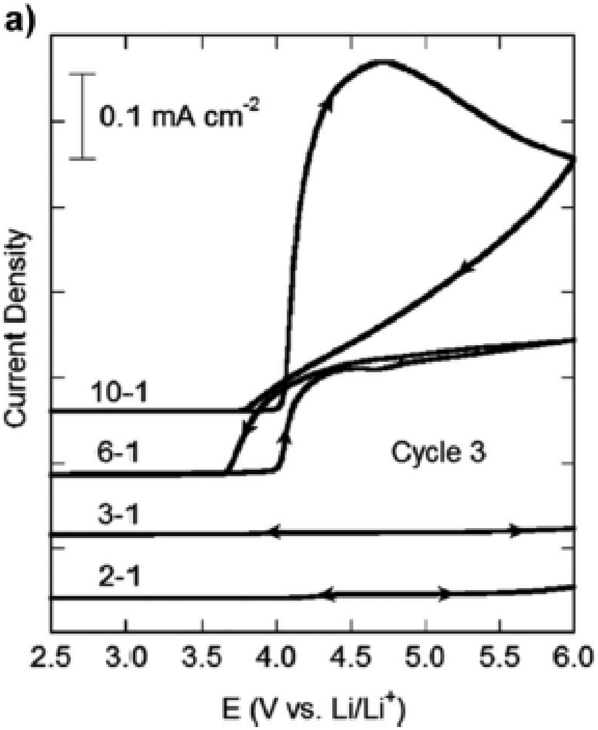
In this situation, we speculate

Highly concentrated electrolytes: some examples



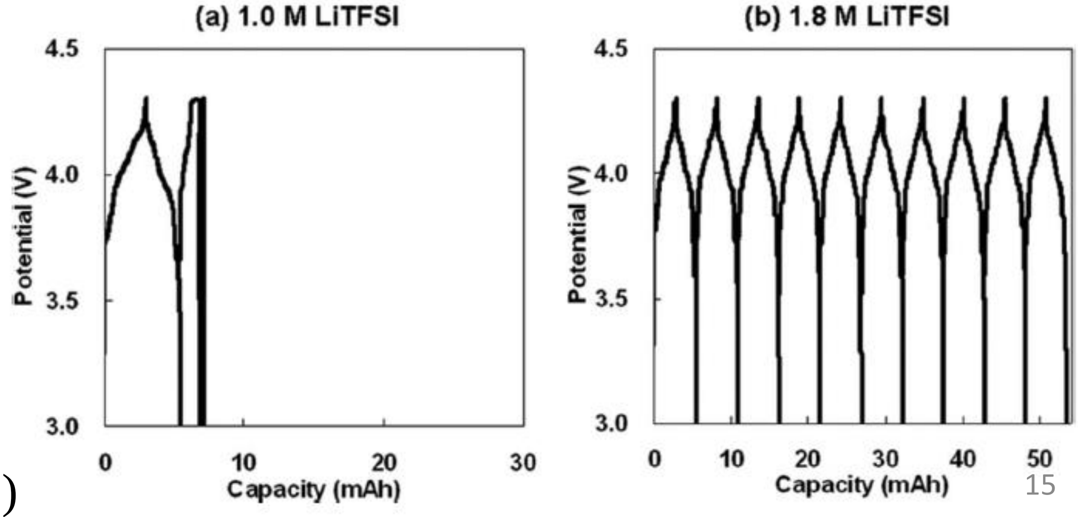
Graphite and Li metal are stable in highly concentrated EC-free electrolytes

Chem. Commun., 2013, **49**, 11194



Al corrosion is suppressed without PF_6 (LiTFSI – EC)

Reversible intercalation into various hosts



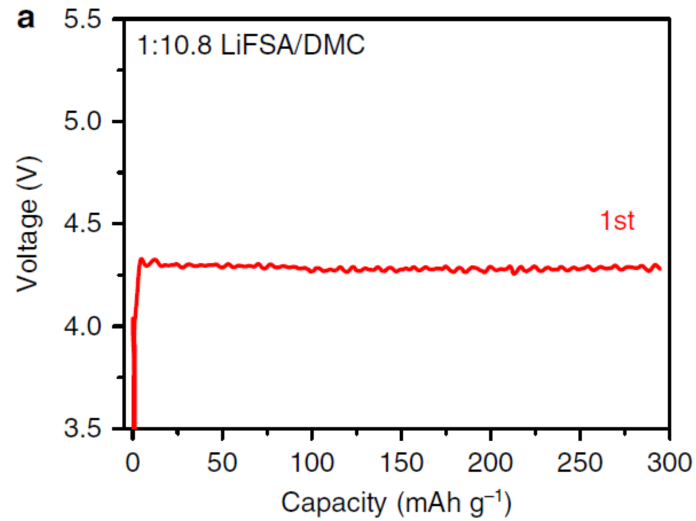
J. Power Sources, **231**, 234 (2013)

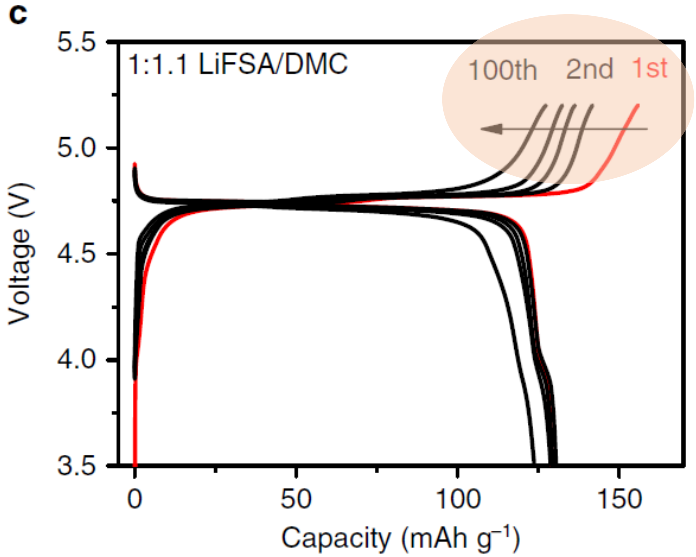
High voltage superconcentrated electrolytes

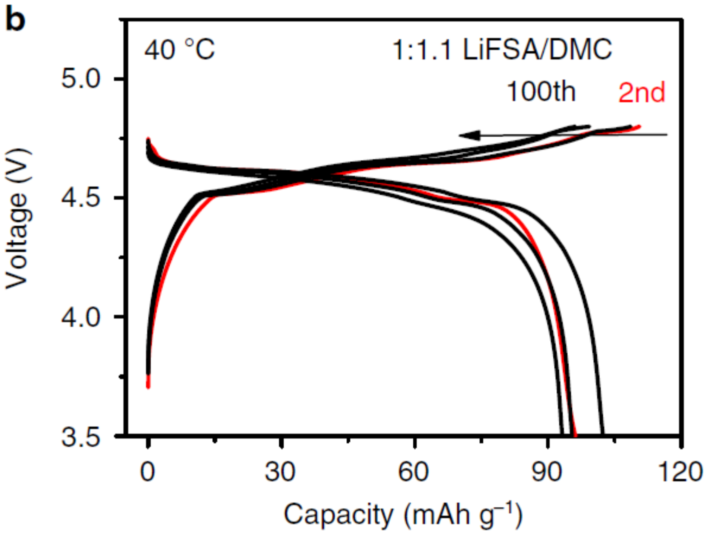
$LiNi_{0.5}Mn_{1.5}O_4$ material at 5 V

J. Wang et. al. *Nature Commun.* 7 (2016) 12032

Capacity on charge is higher than on discharge







We reach the limit of salt solubility, but the electrolyte oxidation is still not suppressed

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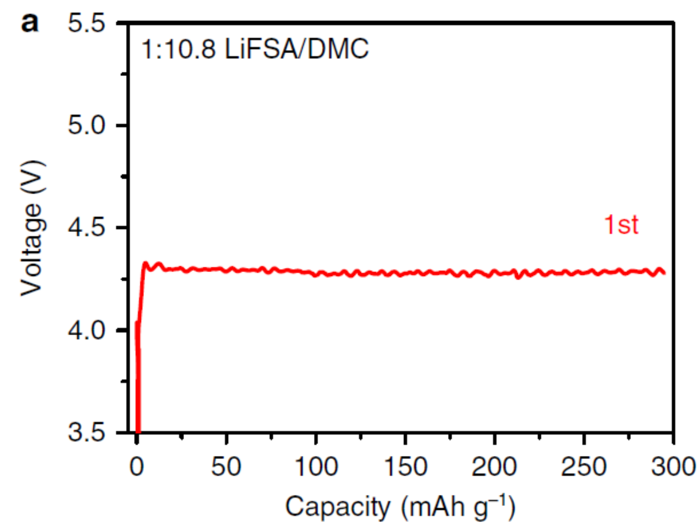

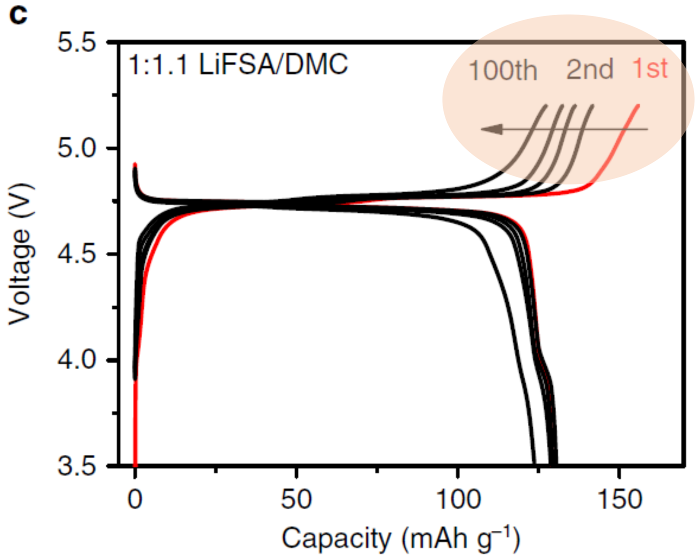

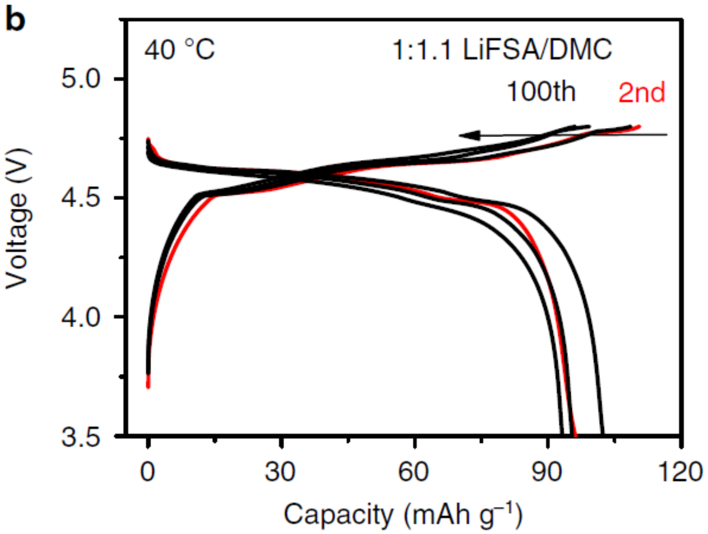

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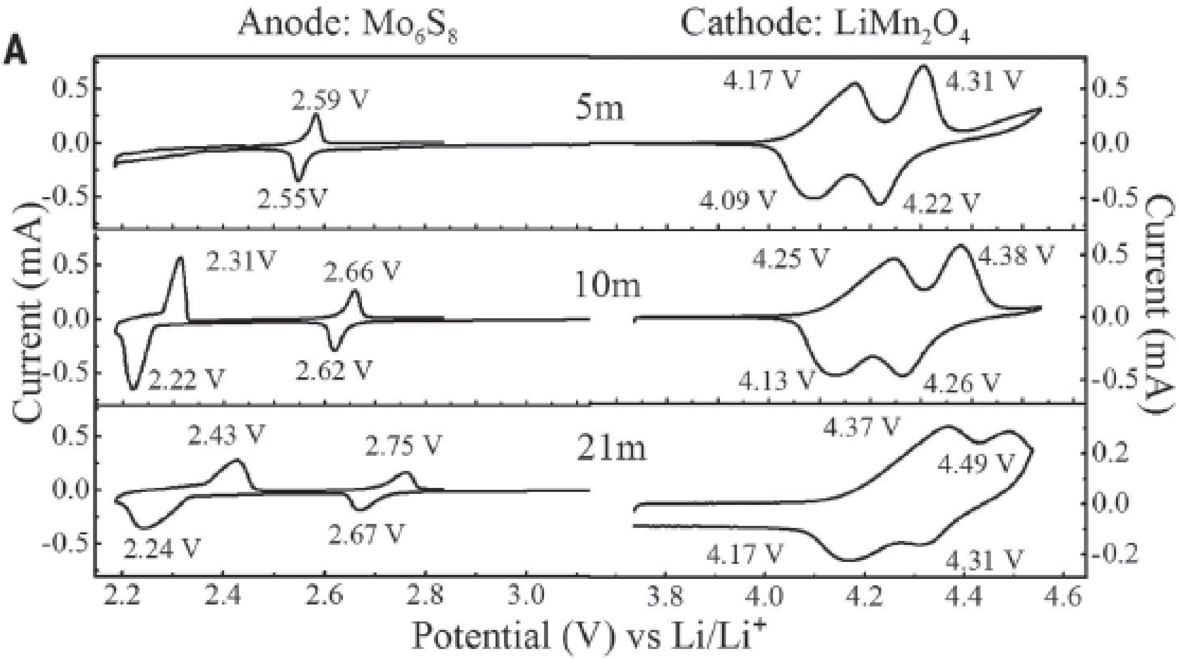
Water-based superconcentrated electrolytes



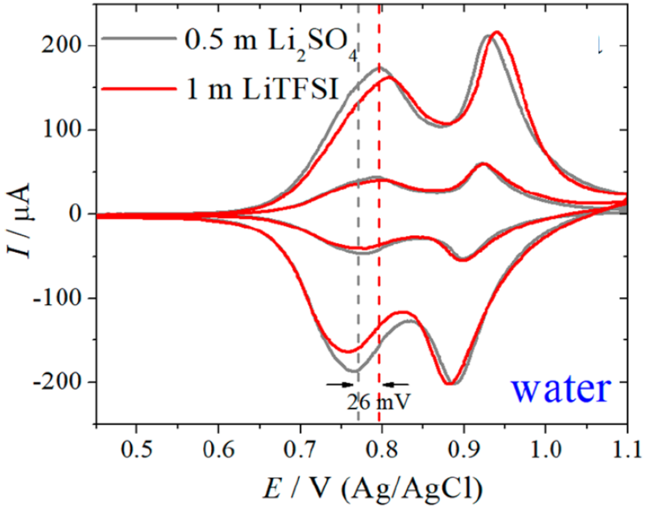
- Increased width of electrochemical window
- Protective layers at cathode and anode
- High conductivity

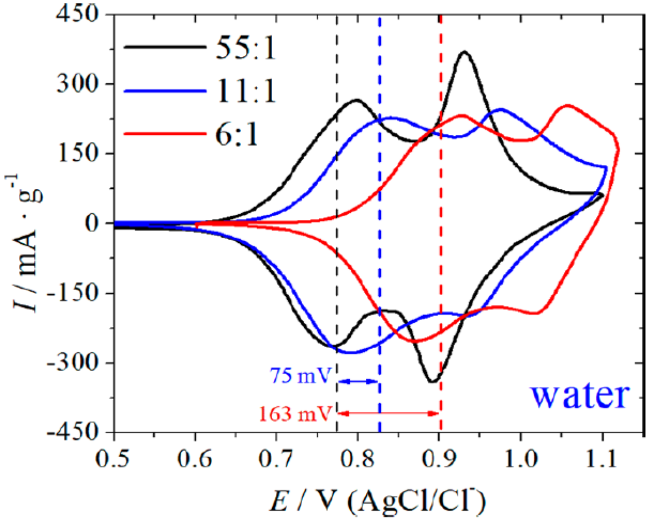
L. Suo et al. Science, 350 (2015) 938 - 943

Disadvantages of superconcentrated electrolytes

1) High cost
2) High viscosity, low conductivity (except for aqueous solutions)
3) Slower intercalation kinetics

II. $LiMn_2O_4$ in aqueous concentrated electrolytes



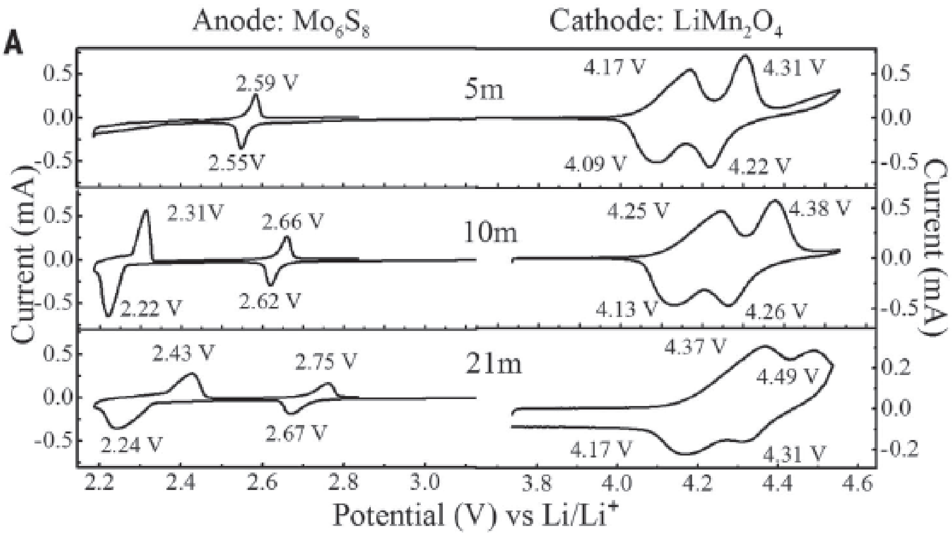


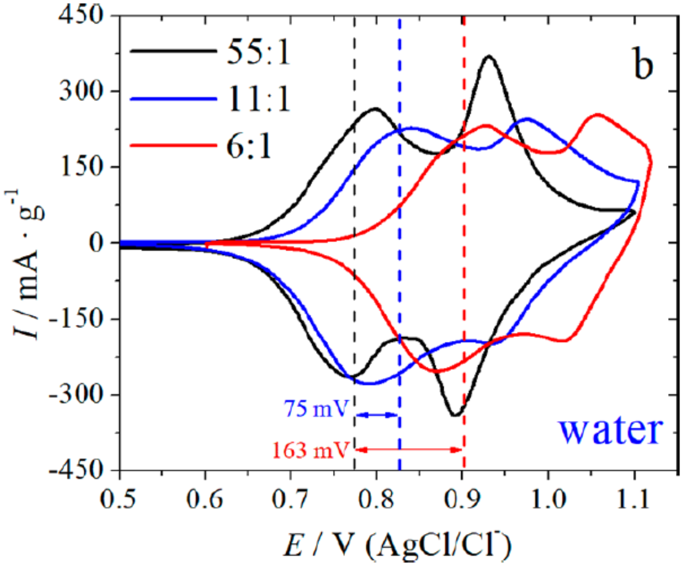
No decrease in the electrolyte decomposition rate

$$\boxed{I = nF\,k\,c(Li^+)}$$

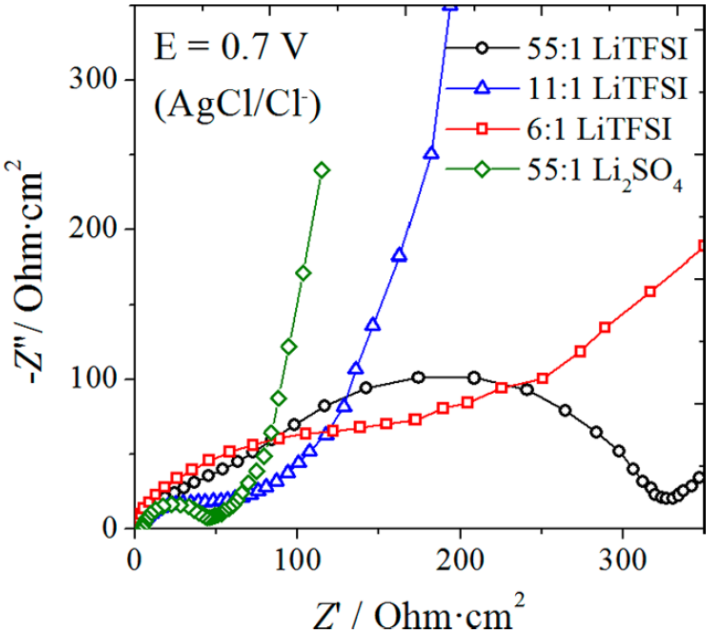
- Li^+ activity increases (formal potentials of the peaks increase)
- The charge transfer kinetics is decreased
- Decrease of D_{app} in LiTFSI solutions

Li^+ activity is increased by 3 orders of magnitude





- Most rapid charge transfer in SO_4^{2-} aqueous solutions
- Slowest kinetics in 1 m LiTFSI (surface dissolution)
- Faster kinetics in 5 m LiTFSI (suppression of surface dissolution)
- Decreased charge transfer rate in 9 m LiTFSI (aqueous CEI?)



- XPS of the cycled electrodes:

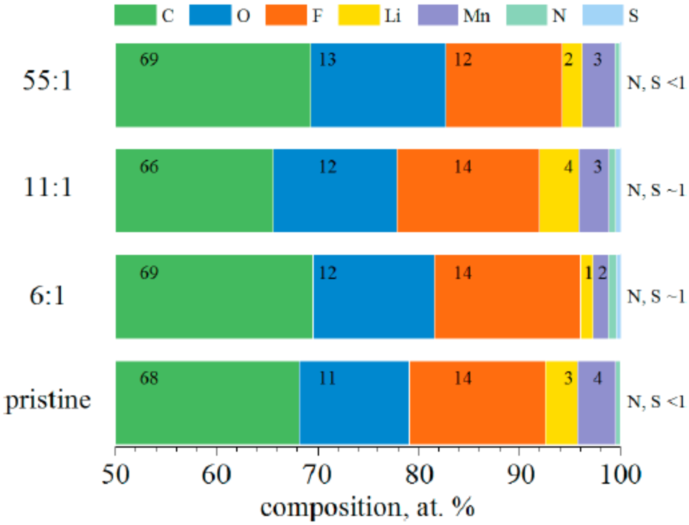
- changes in composition are hard to trace

- EIS analysis:

- very resistive CEI layer in 55:1 LiTFSI (surface defective layer)

- much less resistive CEI layers in 11:1 and 6:1 electrolytes

- High R_{ct} in 6:1 electrolyte



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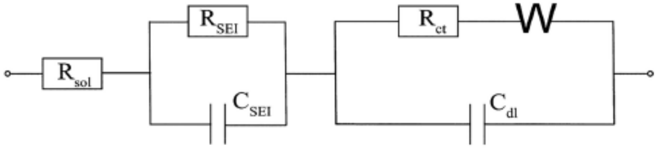
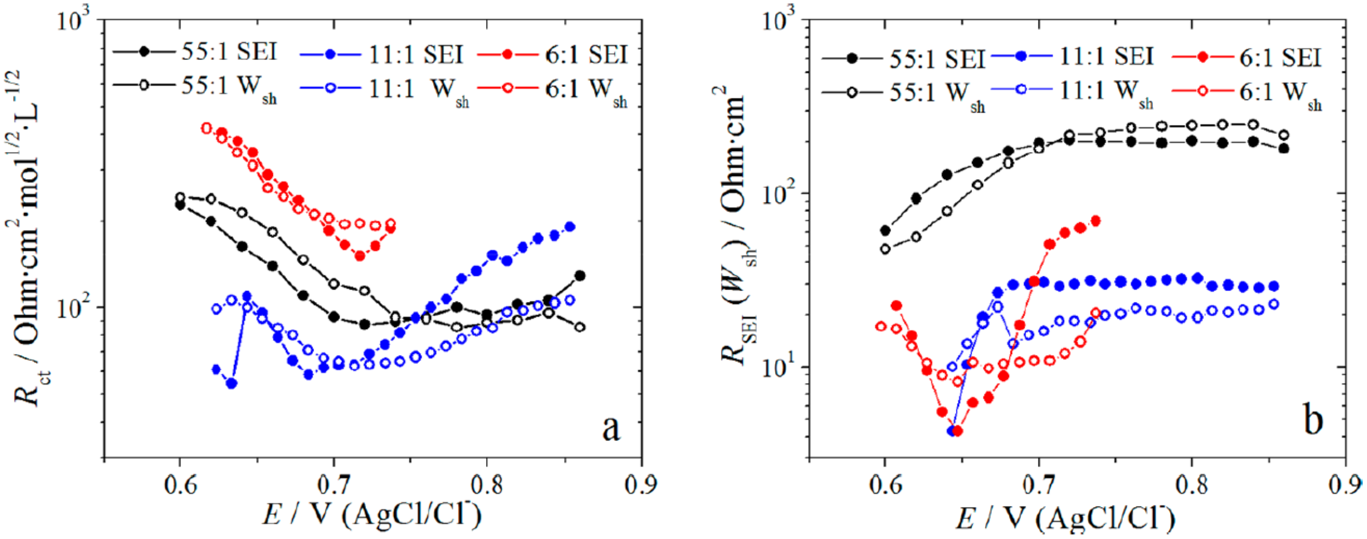
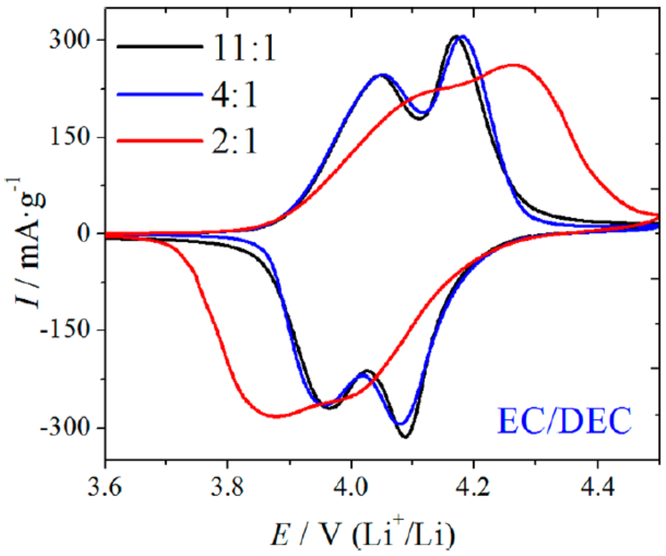
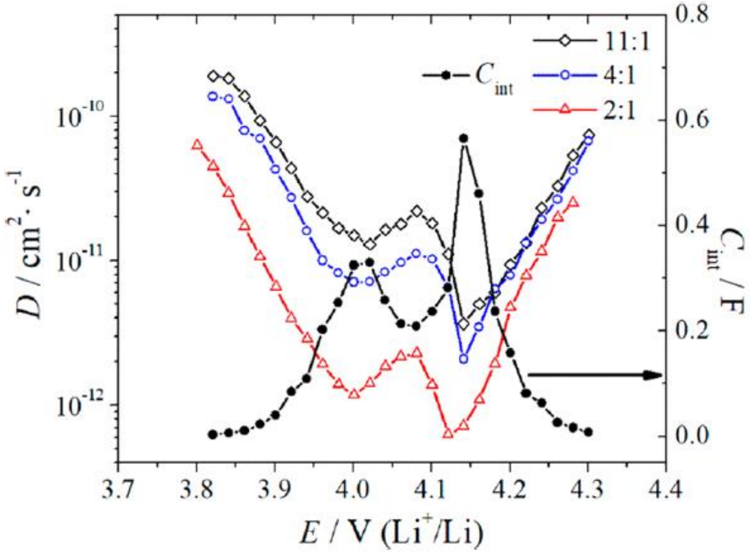


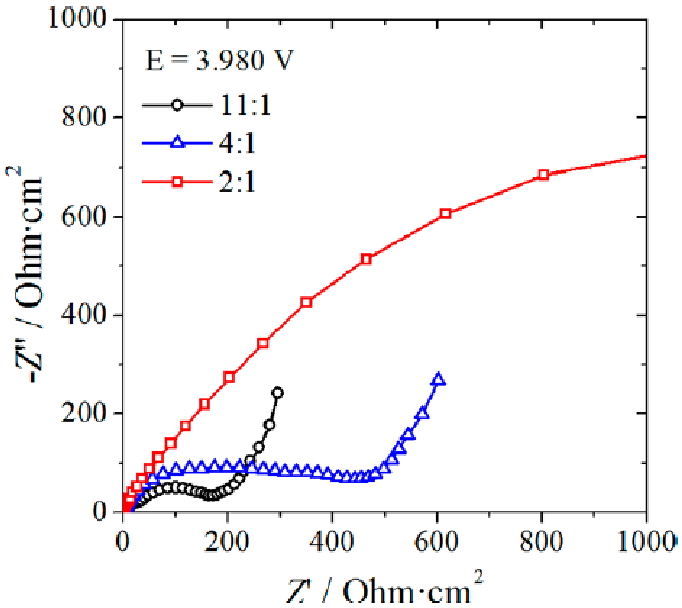


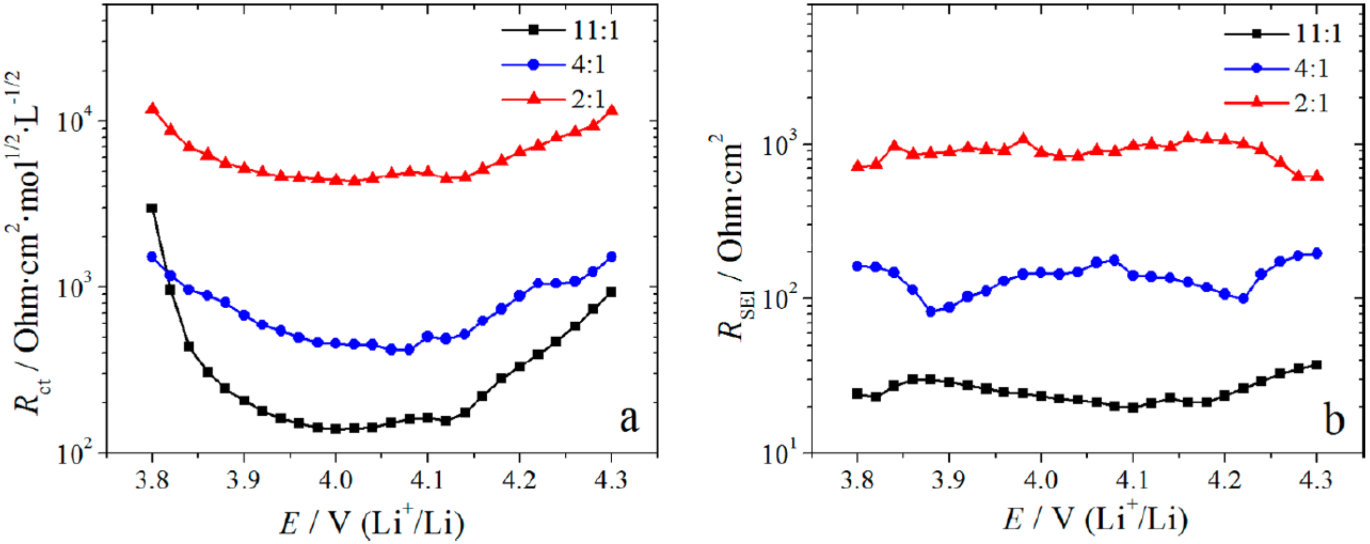
EC-based superconcentrated electrolytes

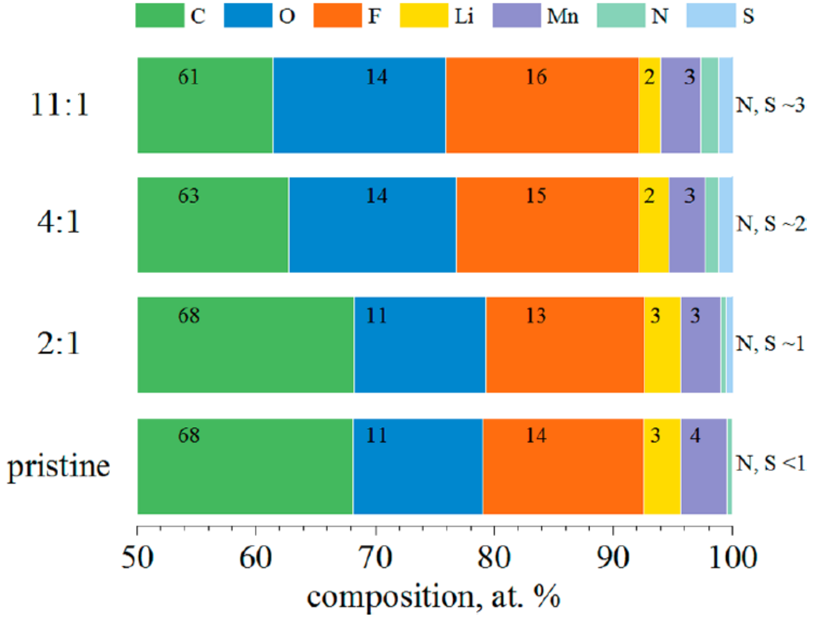




- Close charge transfer rates in 11:1 and 4:1 solutions
- Very slow kinetics in 2:1 solutions
- CEI formation in all solutions
- One order of magnitude drop in D_{app}







- No signs of salt decomposition on cathode
- $R_{ct}(2:1) > R_{ct}(4:1) > R_{ct}(11:1)$
- $R_{CEI}(2:1) > R_{CEI}(4:1) > R_{CEI}(11:1)$

Conclusions on the superconcentrated electrolytes

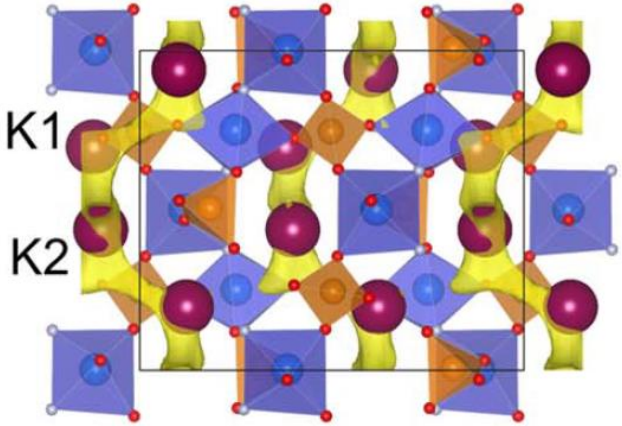
- In **aqueous** solutions, the highest charge transfer rates are observed for intermediate concentrations (where surface dissolution for $LiMn_2O_4$ is suppressed)
- At higher concentrations the reaction is slowed down (aqueous CEI? Salt precipitation?)

- In **carbonate** electrolytes, the resistance of surface layers increases with the increase in concentration (CEI formation)
- Charge transfer rates decrease with the increase in surface layers resistance

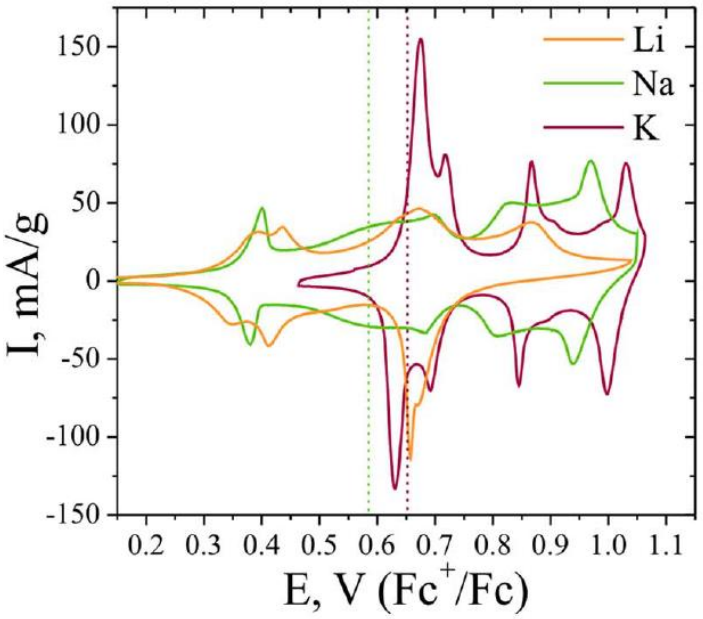
Higher interfacial stability will be compensated by slower kinetics

V. Nikitina et al. *Langmuir* (2017) 10.1021/acs.langmuir.7b01016

High voltage potassium batteries: the EEI structure effects



K 1D



$AVPO_4F$ ($A = Li^+, Na^+, K^+$)

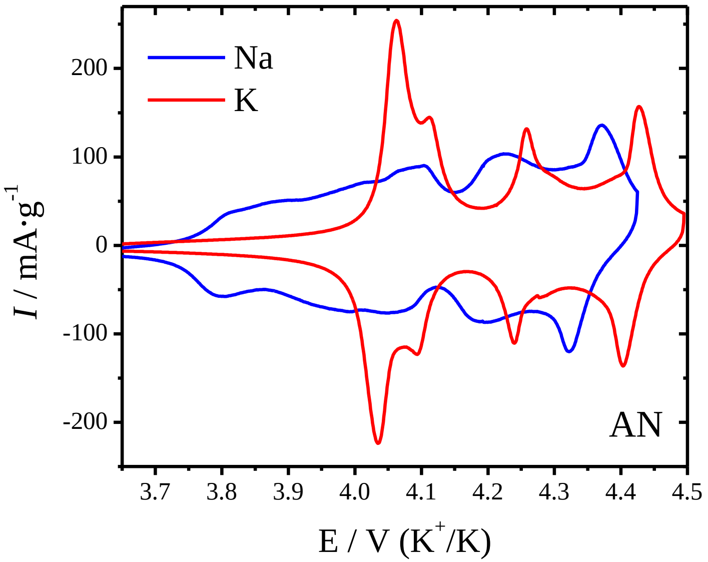
nearly perfect framework for K

What factors determine the differences in charge transfer kinetics for different alkali metal ions?

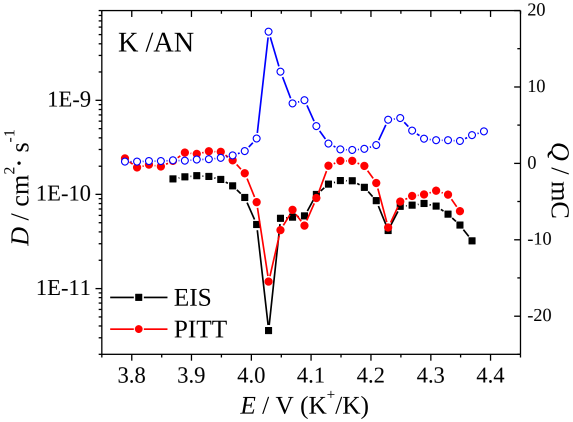
We can compare intercalation rates for **Na^+** and **K^+** (same intercalation sites)

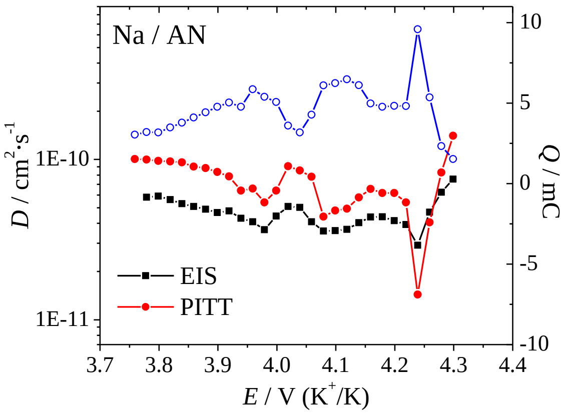
A perfect model system - a system with the simplest possible EEI structure

Acetonitrile – no CEI formation, but some material dissolution

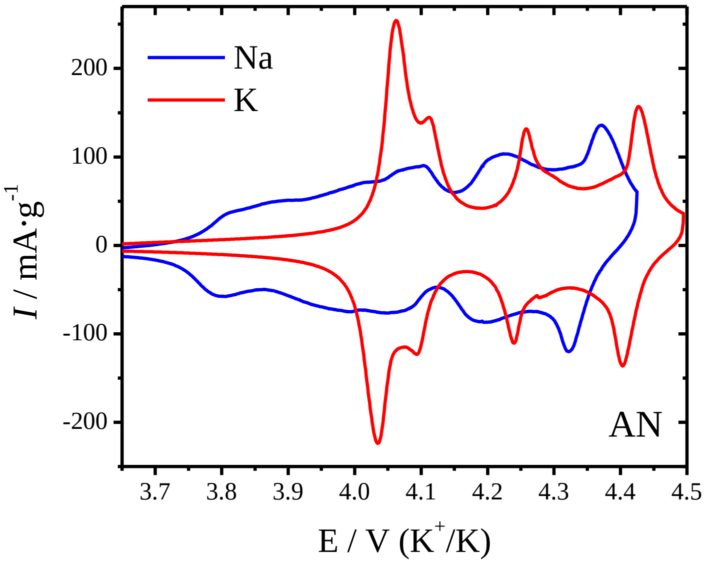


Fast diffusion of Na$^+$ and K$^+$

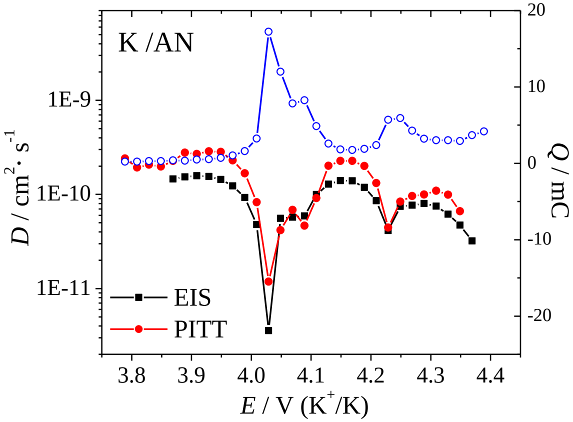


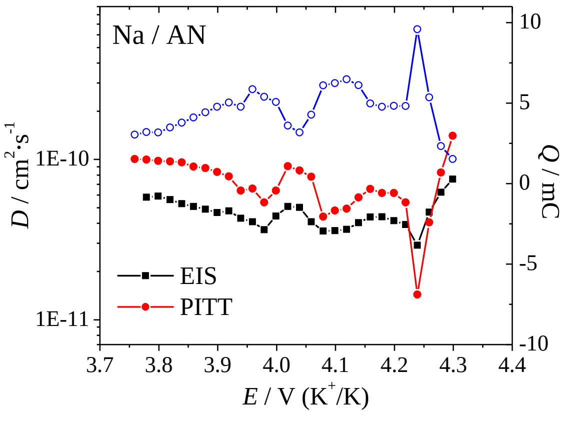


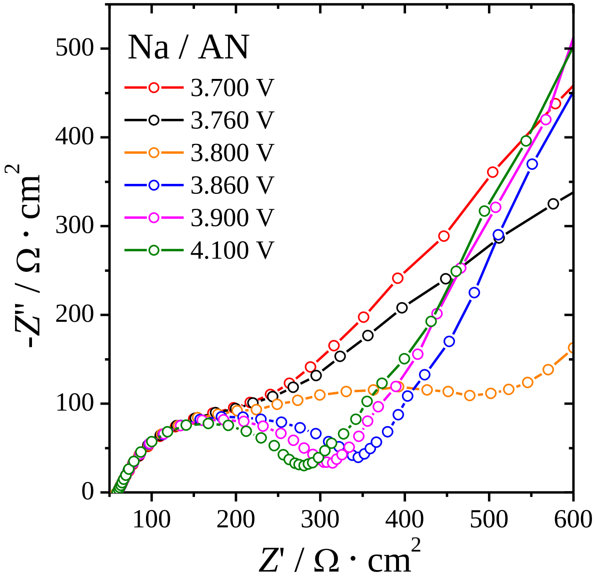
Acetonitrile – no CEI formation, but some material dissolution

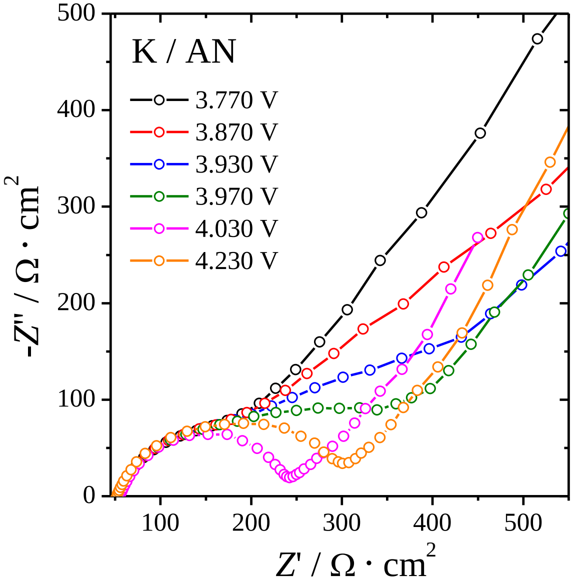


Fast diffusion of Na^+ and K^+





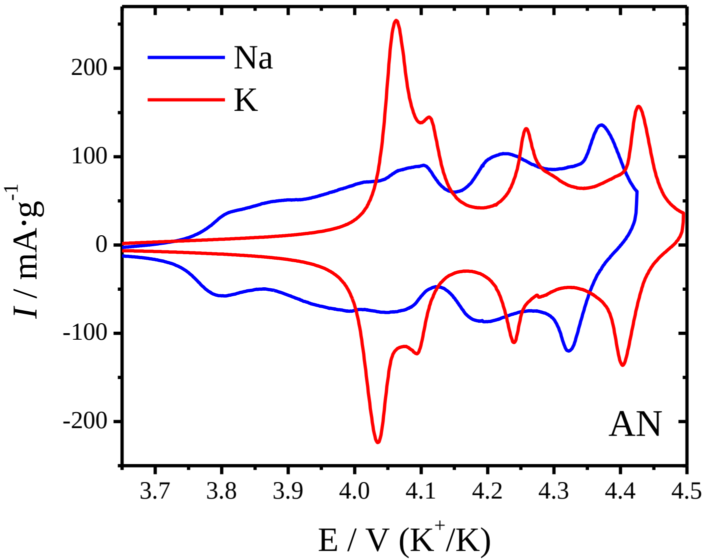




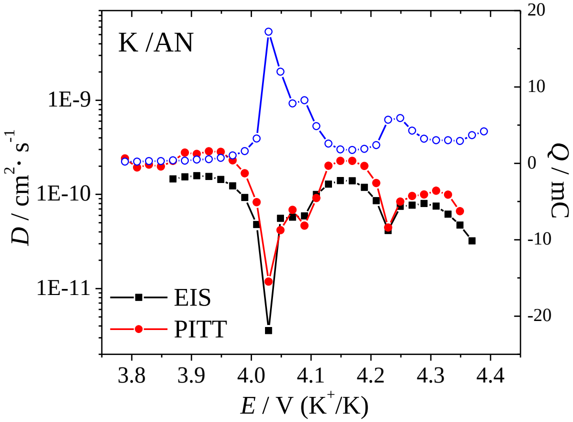
Very fast (de)insertion kinetics (barely measurable with EIS)

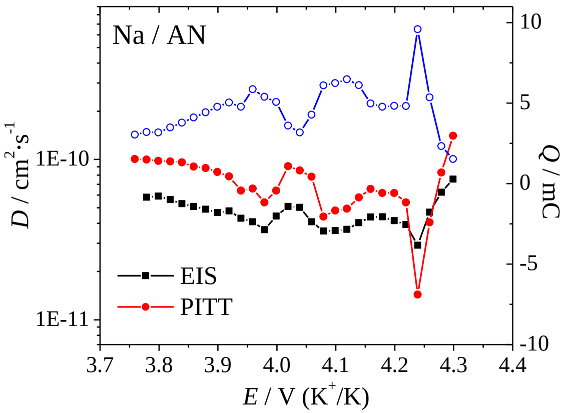
- reduced A^+ concentration
- very low material loadings
- Ag^+/Ag RE

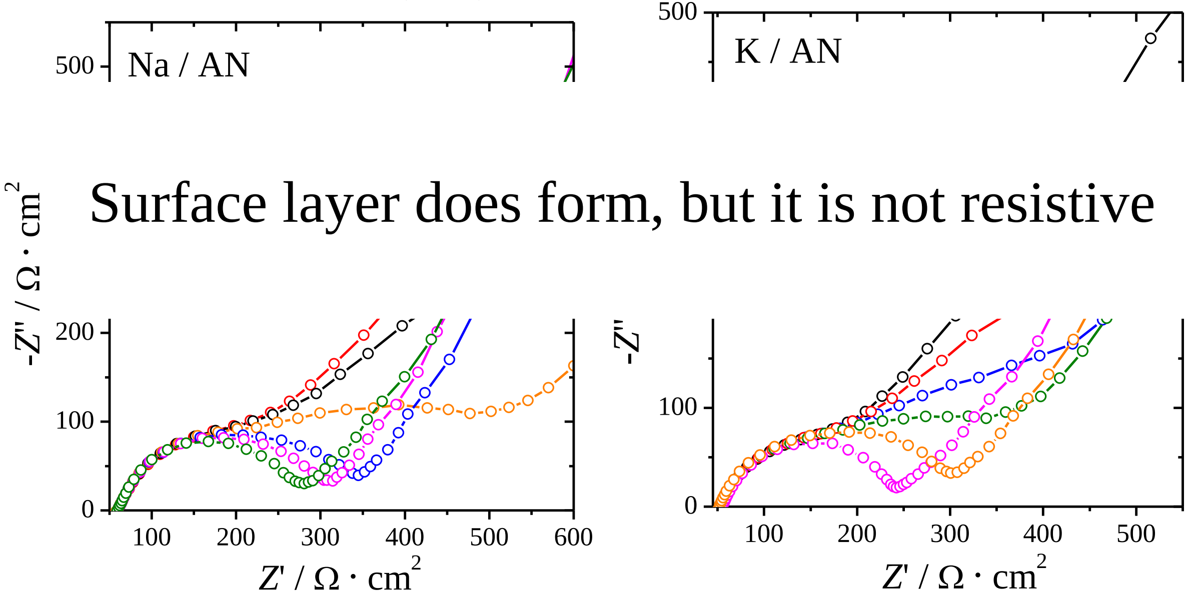
Acetonitrile – no CEI formation, but some material dissolution



Fast diffusion of Na^+ and K^+





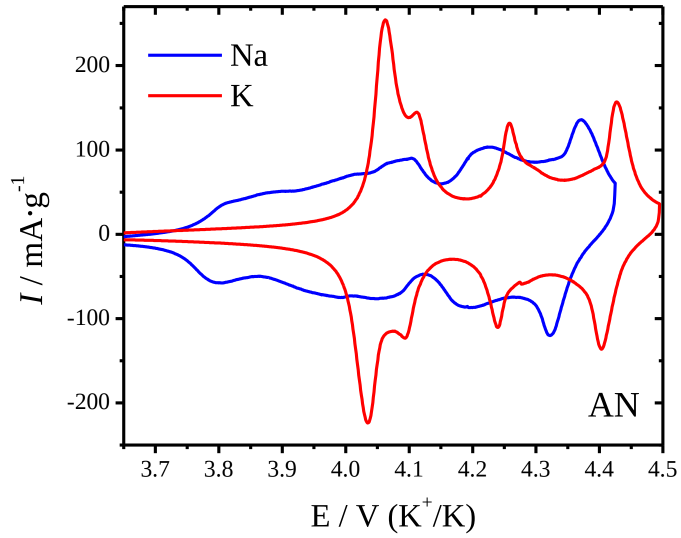


Surface layer does form, but it is not resistive

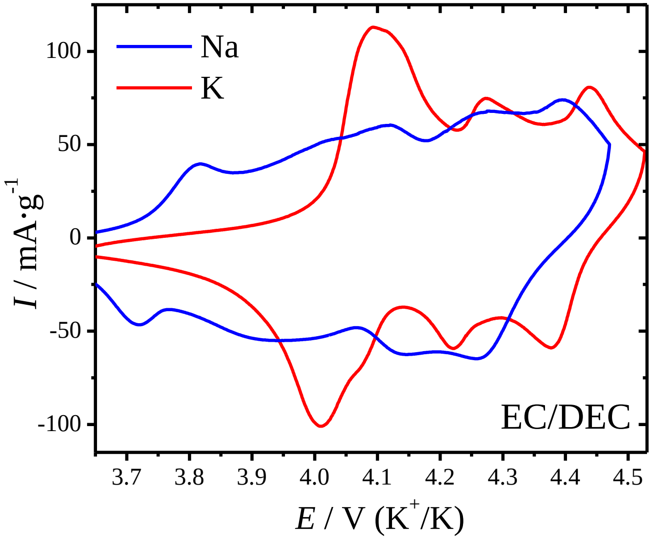
Very fast (de)insertion kinetics (barely measurable with EIS)

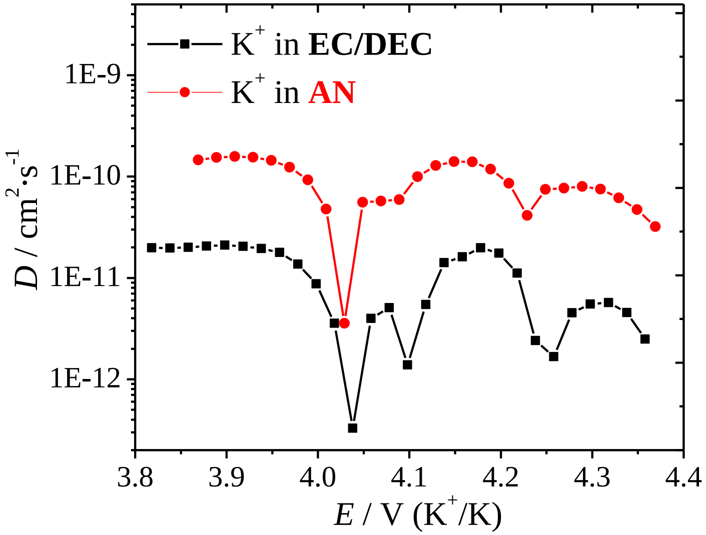
- reduced A^+ concentration
- very low material loadings

What happens when a thicker CEI layer forms?

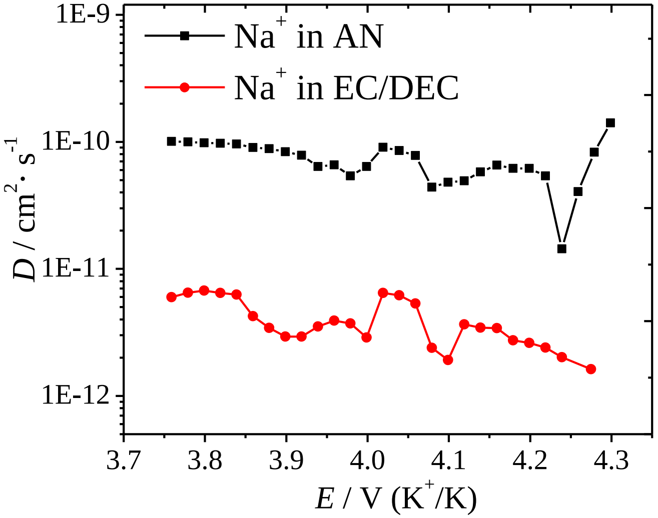


- CV peaks become broader
- Peak-to-peak separations increase





- D values decrease by one order of magnitude
- The difference is higher for Na$^+$

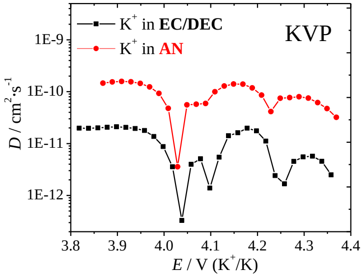


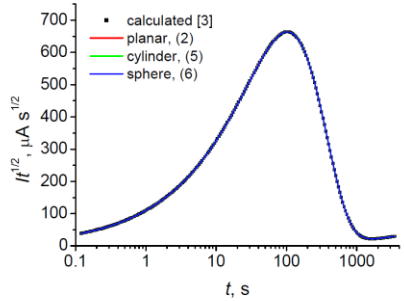
Why do D values change?

Inadequate method of calculating D?

- Finite diffusion, low amplitude potential steps, single phase regions, narrow particle size distribution, correct choice of diffusion geometry, account for ohmic drop and slow kinetics (C. Montella)

$$I(t) = 2\frac{\Delta Q}{\tau}\sum_{n=1}^{\infty}\frac{\Lambda^2}{\Lambda^2+\Lambda+b_n^2}\exp\left(-\frac{b_n^2 t}{\tau}\right)$$





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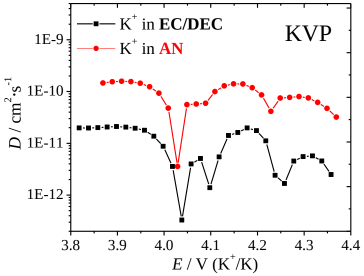
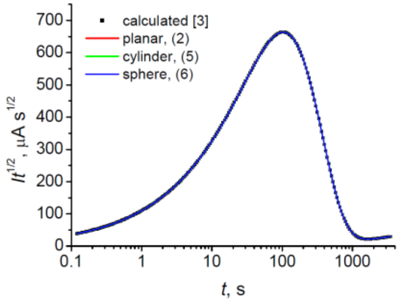
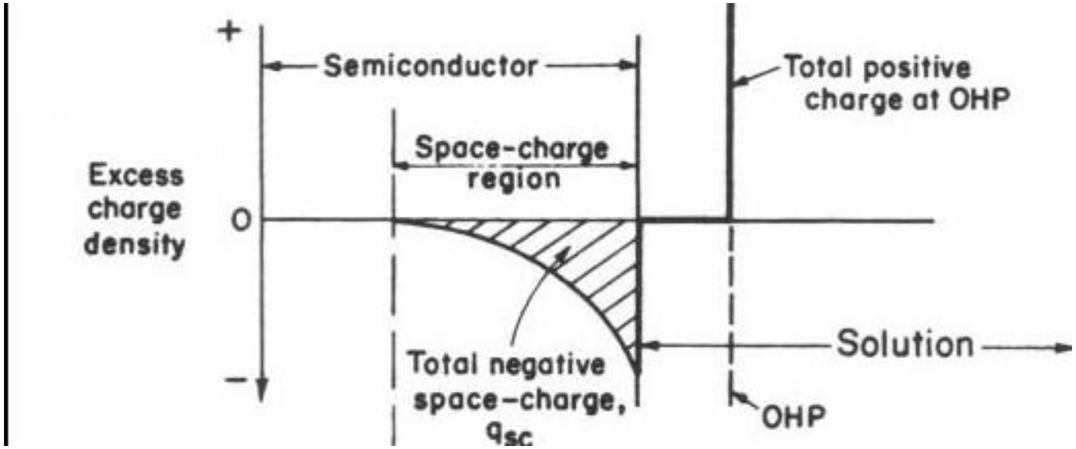
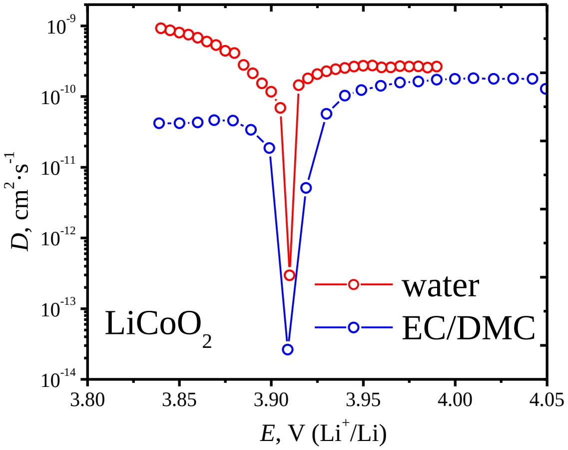


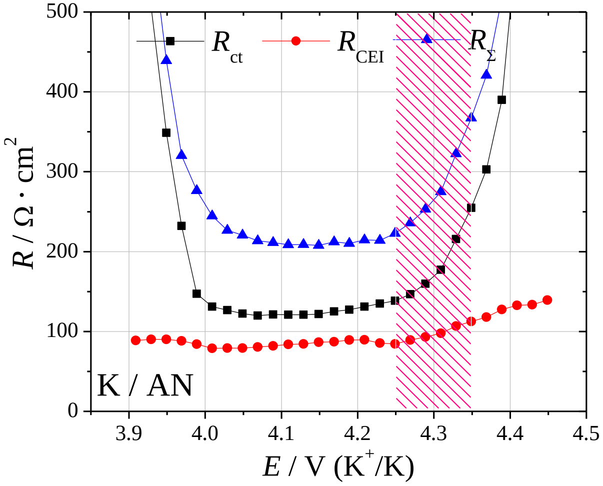


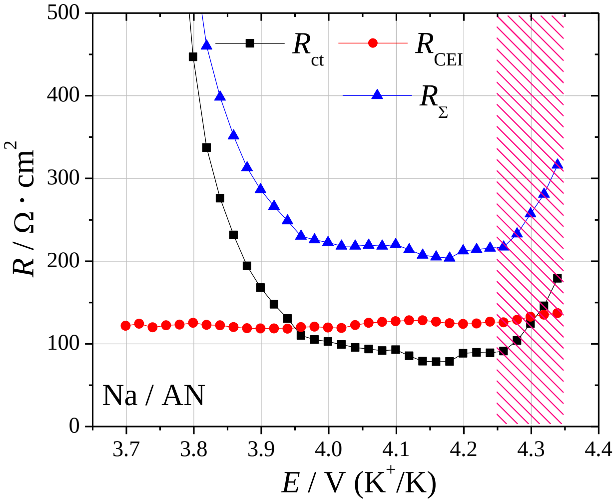
Most cathode materials are semiconductors

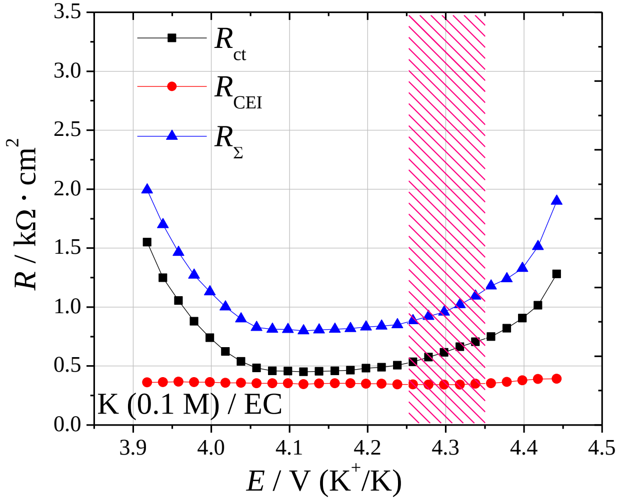


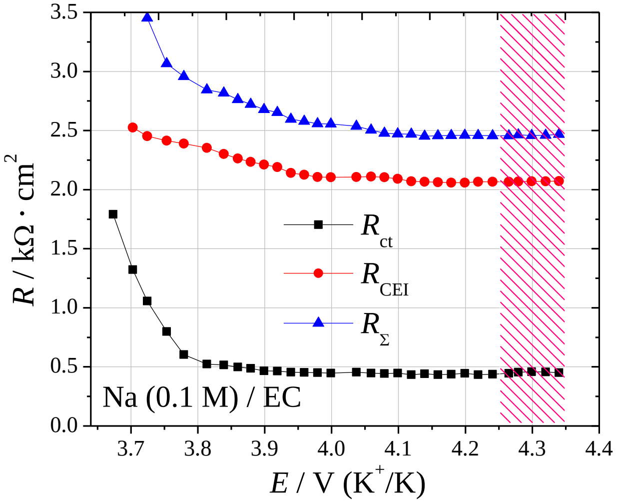


What about charge transfer rates for K^+ and Na^+?









- In AN:

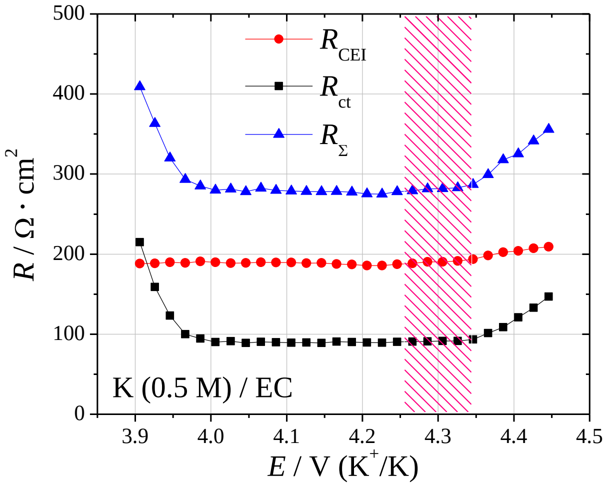
R_{ct} values for Na^+ and K^+ are close

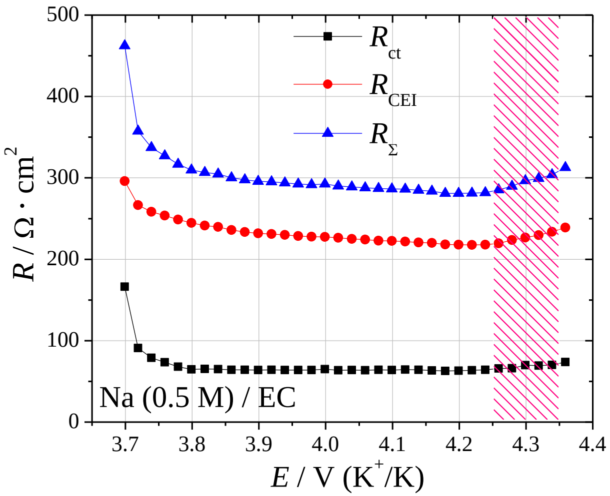
- In EC/DEC:

R_{ct} values for Na^+ and K^+ are close, but R_{CEI} are higher for Na^+

Less resistive CEI layers are formed in K^+ electrolytes?

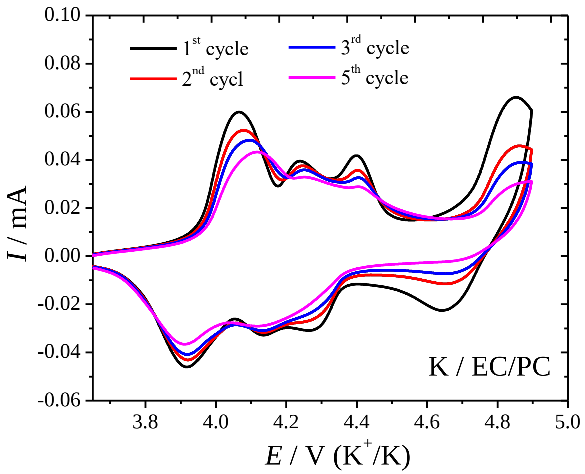
If we increase KPF$_6$ concentration:

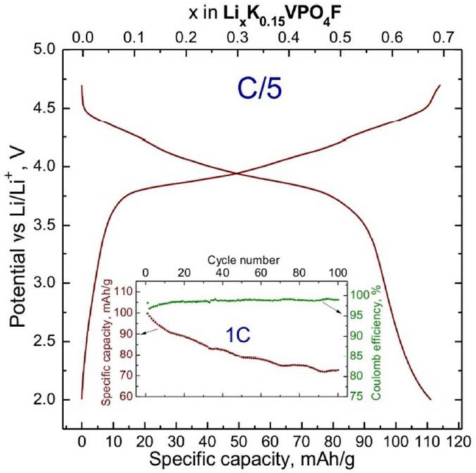




- In 0.5 M KPF$_6$ in EC/DEC:

R$_{ct}$ values are higher for K$^+$, while R$_{CEI}$ values are still lower than for Na$^+$



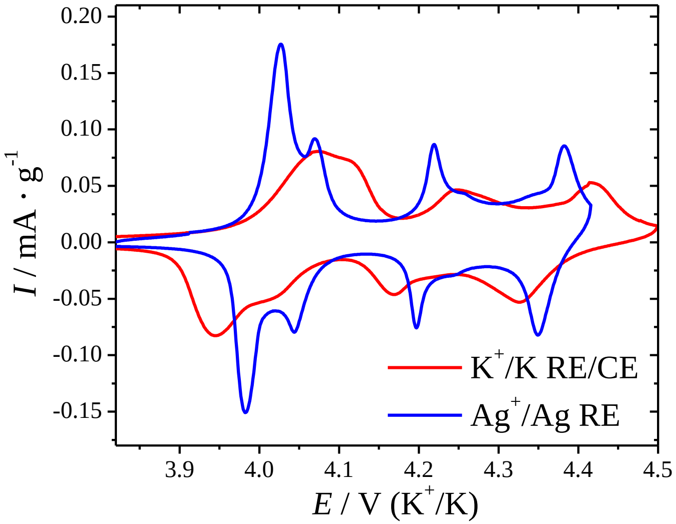


Less resistive CEI layers are formed in K$^+$ electrolytes (higher K$^+$ salt solubility), but the **charge transfer resistance is higher** (large size of the cation)

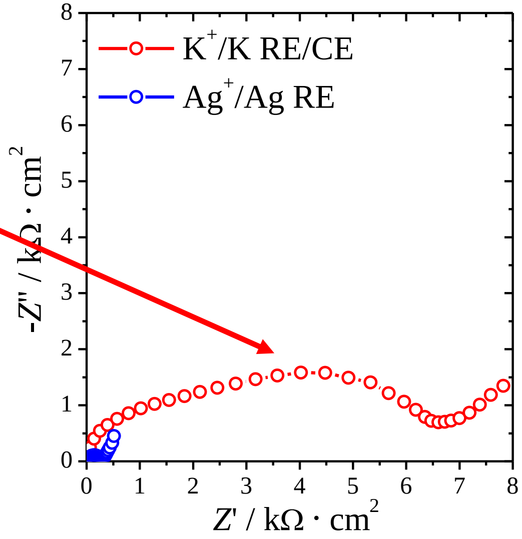
S. Fedotov et al. *Chem. Mater.*, 28 (2016) 411

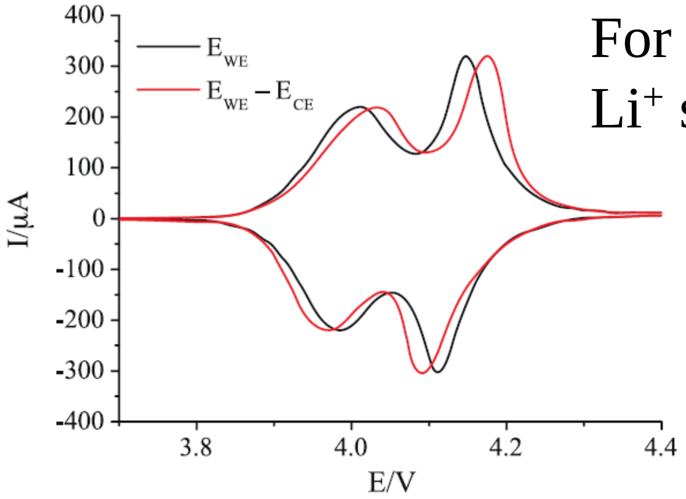
The feasibility of a high voltage K^+ battery

We can’t use metallic K anode



Extremely large kinetic polarization





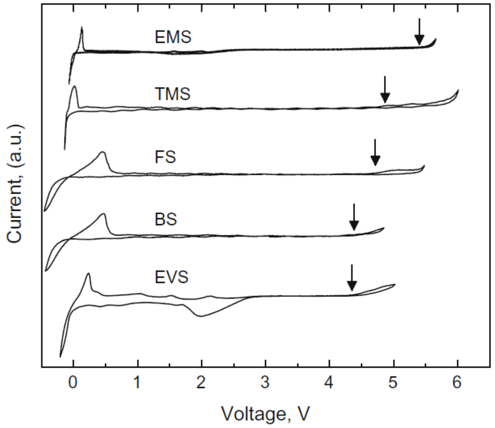
For comparison:
Li^+ system

The need for a stable anode and a high voltage electrolyte

S. Vassiliev et al. *Electrochim. Acta* 190 (2016) 1087

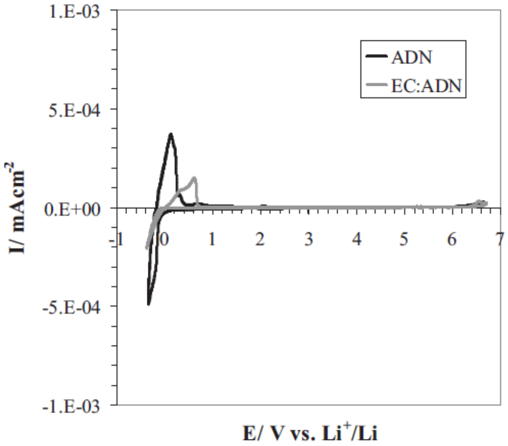
High voltage electrolytes for K-ion batteries

Sulfone

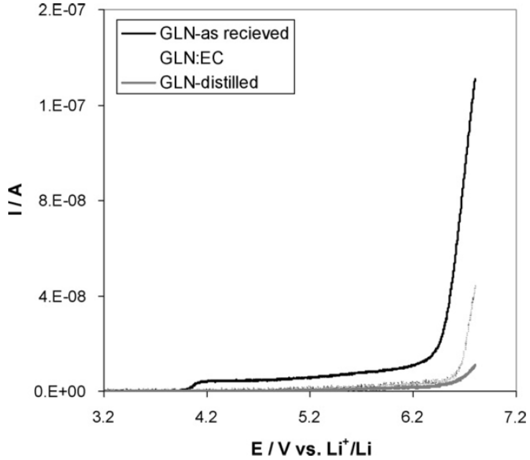


A. Abouimrane et al. *Electrochem. Commun.* 11 (2009) 1073

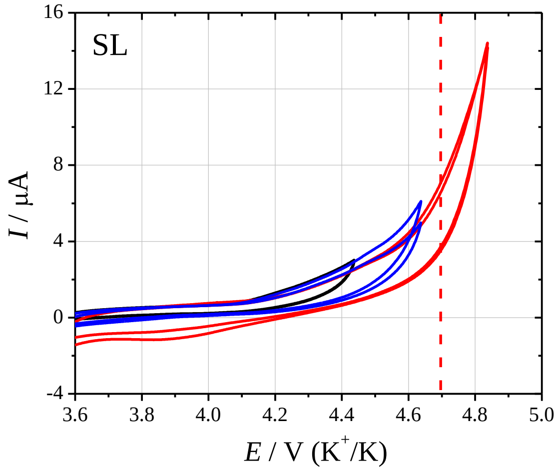
Nitriles

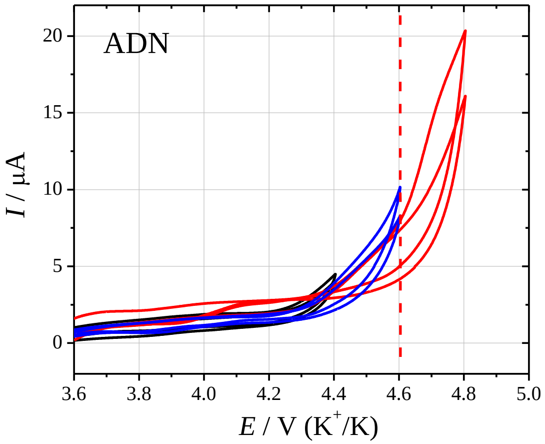


Y. Abu-Lebdeh et al. *J. Electrochem. Soc.* 156 (2009) A60



Y. Abu-Lebdeh et al. *J. Power Sources.* 189 (2009) 576





High voltage electrolytes for K-ion batteries

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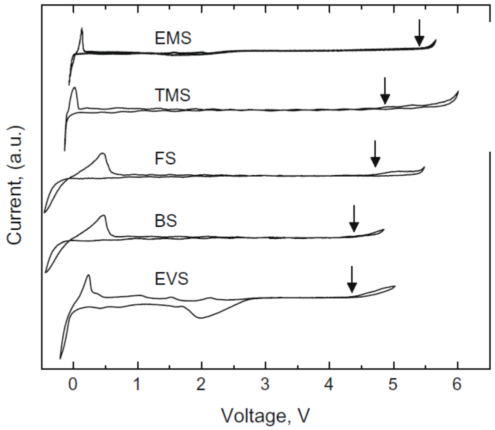
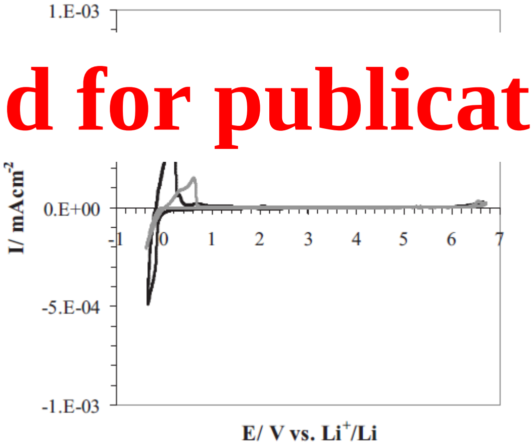


A. Abouimrane et al. *Electrochem. Commun.* 11 (2009) 1073



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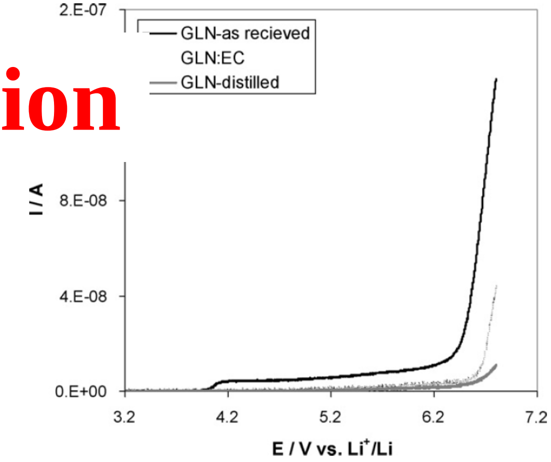
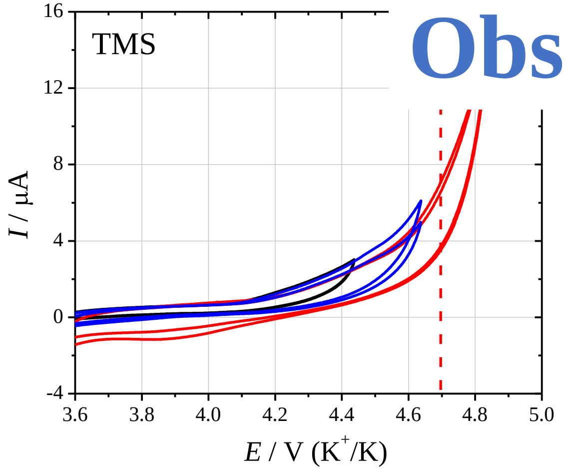
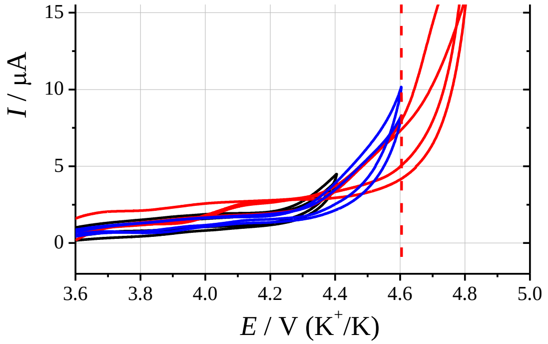


Y. Abu-Lebdeh et al. *J. Power Sources.* 189 (2009) 576

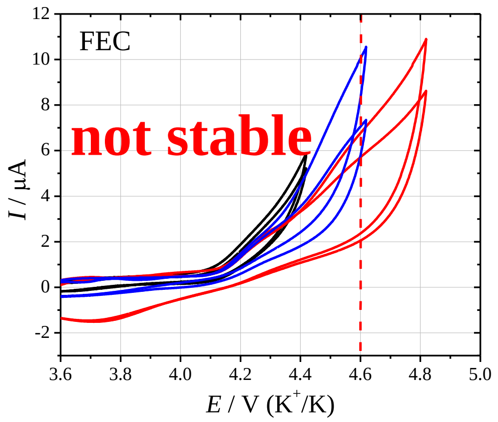
Good for publication

Observed in real life

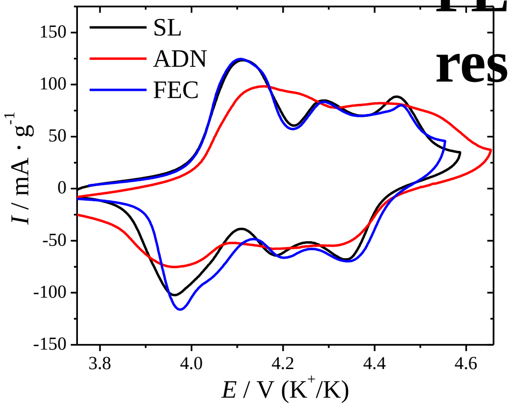


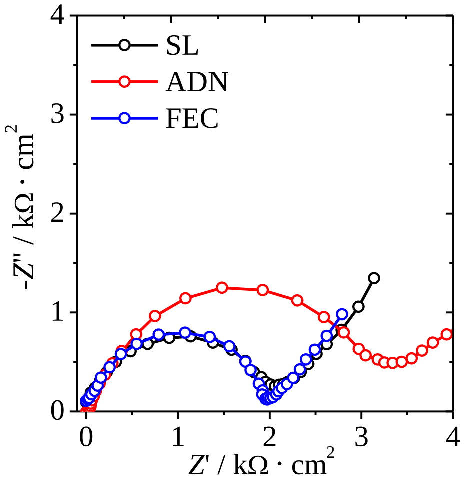


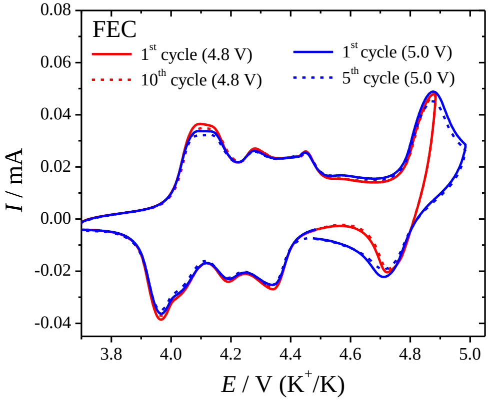
FEC – lowest R_{ct} resistance + high R_{CEI}

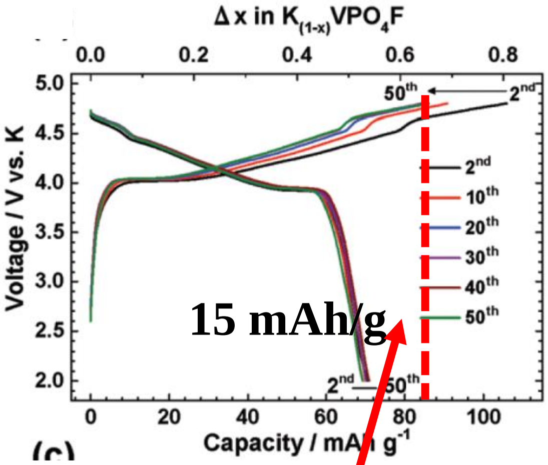


not stable

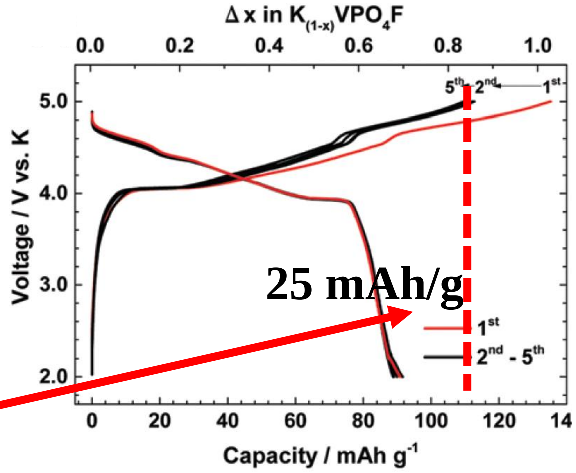






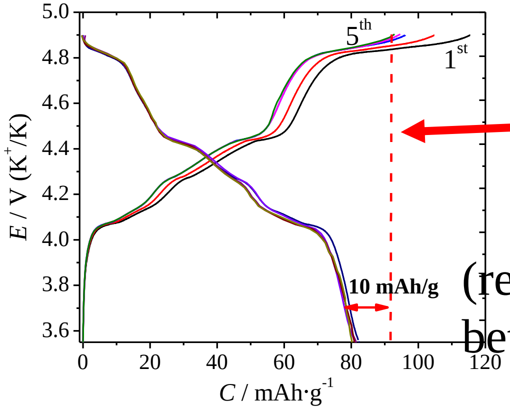


15 mAh/g



25 mAh/g

"Stable" cycling up to 4.8 V, **but:**



10 mAh/g

(results should be better in a 2-el cell)

The problem is not solved

K. Chihara et al. *Chem. Commun.*, 2017, 53, 5208

Thank you for your attention!

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L.V. Yashina (MSU)
S.M. Kuzovchikov (MSU)
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