# Spectroelectrochemical methods in battery research

Modern methods in heterogeneous catalysis

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# Different types of batteries

Primary battery

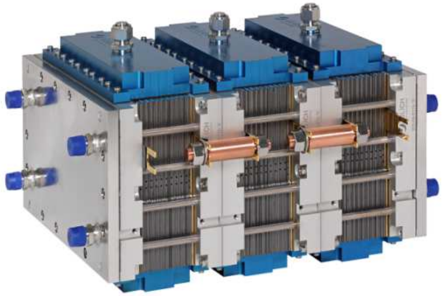
- Zinc-carbon battery
- Alkaline (Zn|$MnO_2$)
- Nickel oxohydride
- Lithium battery
- . . .

Secondary battery

- Lead-acid battery
- Nickel-Cadmium battery
- Nickel-metalhydride battery
- Nickel-zinc battery
- Lithium-ion battery
- Lithium polymer battery
- Lithium-sulfur battery
- Lithium-air battery
- Sodium-sulfur battery
- . . .

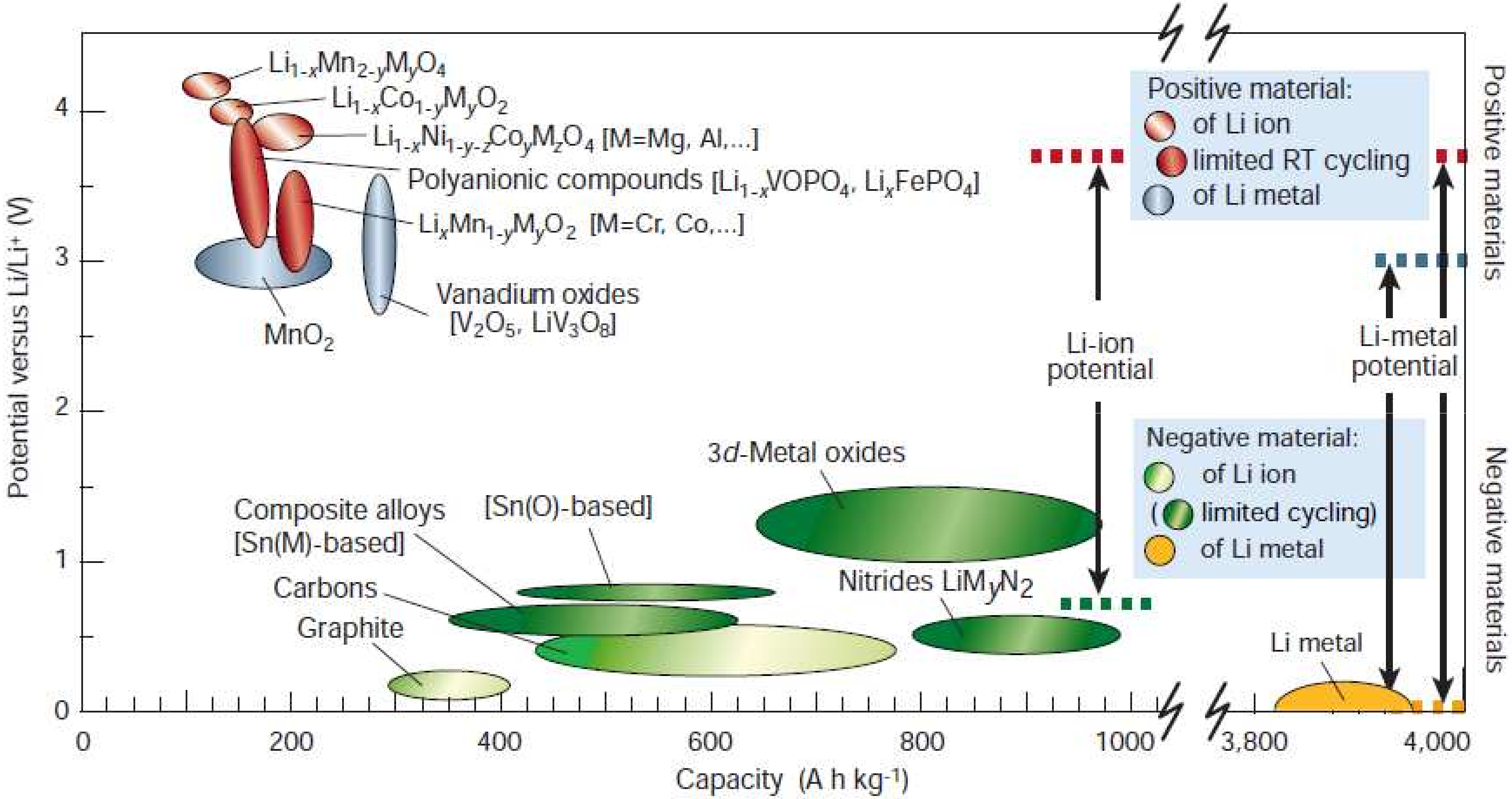
Ternary battery

- Redox-flow battery
- Fuel cell



www.varta.de

# Electrode materials of interest (Li-ion)



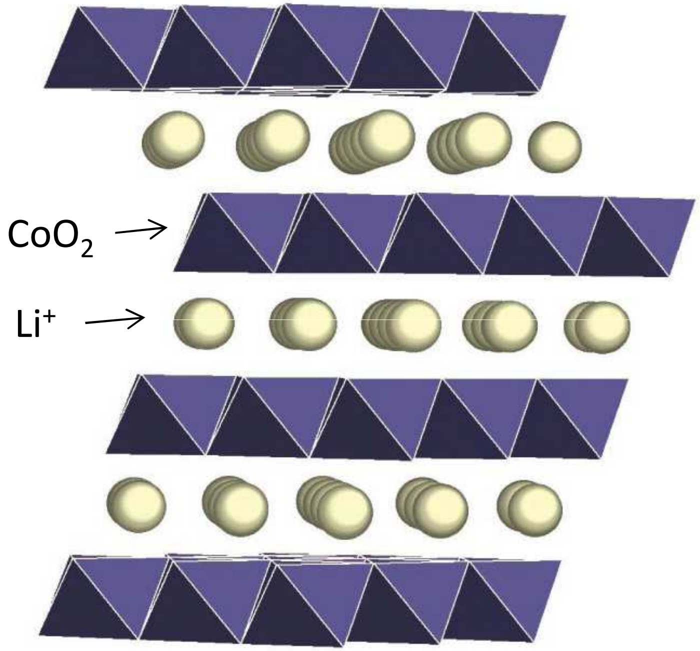
Tarascon et al., Nature 1414 (2001) 359

# Cathode materials (Li-ion)

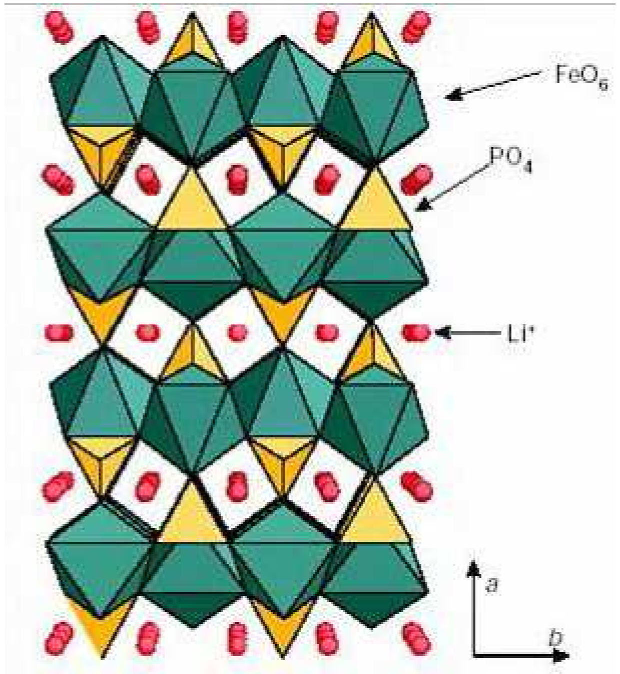
## Structure

Layered Electrodes

Electrodes with channels



Shao-Horn et al., nature materials 2 (2003) 464



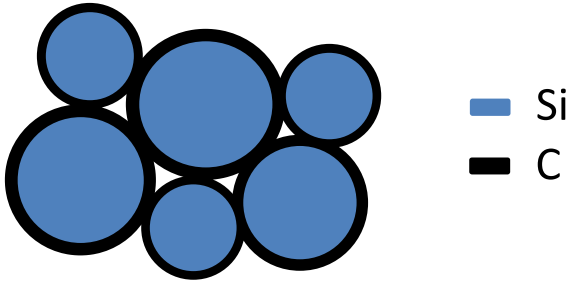
Tarascon et al., Nature 1414 (2001) 359

$LiCoO_2$, $LiNiO_2$
Graphite

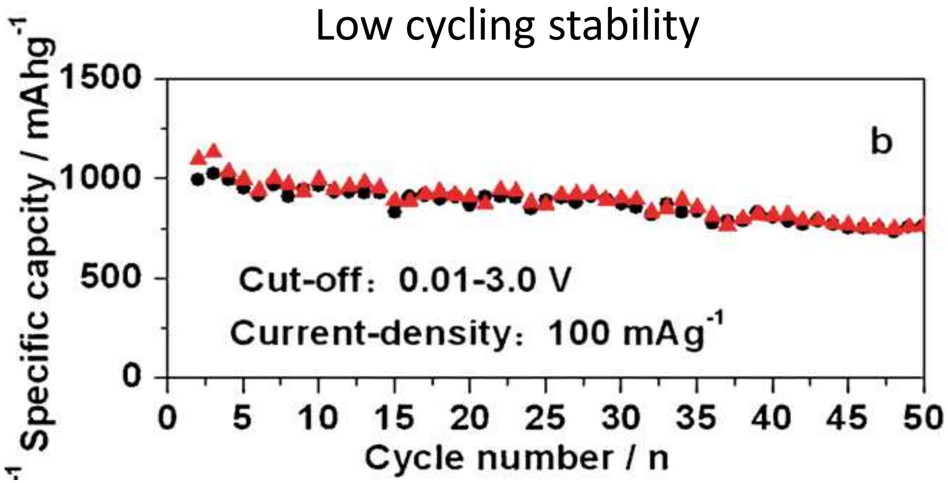
Polyanions (e.g. $LiFePO_4$)
Spinel (e.g. $LiMn_2O_4$)

# Silicon as anode material (Li-ion)

| | Phase | theor. Capacity | Volume change |
|---|---|---|---|
| Graphite | $LiC_6$ | 372 mAh/g | 12% |
| Silicon | $Li_{21}Si_5$ | 4010 mAh/g | 297% |



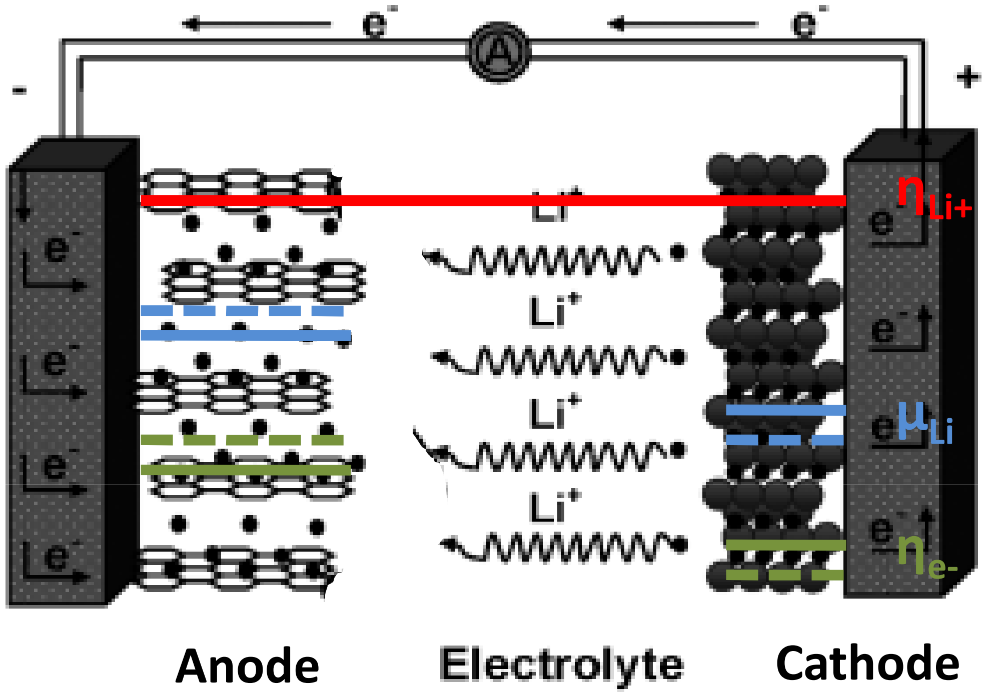
Embedding Si nanoparticles in carbon to compensate for volumechanges



Low cycling stability

J. Power Sources 196 (2011) 4811

# Battery (operational principle)



$$Li \Leftrightarrow Li^{+} + e^{-}$$

$$\eta_i = \mu_i + z_i q \varphi$$

$$\eta_{Li^{+}} = \mu_{Li} - \eta_{e^{-}}$$

$$\mu_i = \mu_i^{0} + kT \cdot \ln(a_i)$$

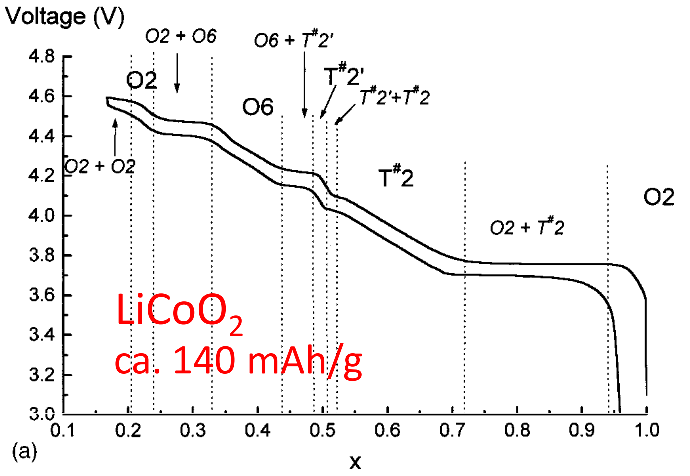
# Electrochemical methods

Battery cycling (galvanostatic)

→ Determination of the capacity and observation of phase transitions

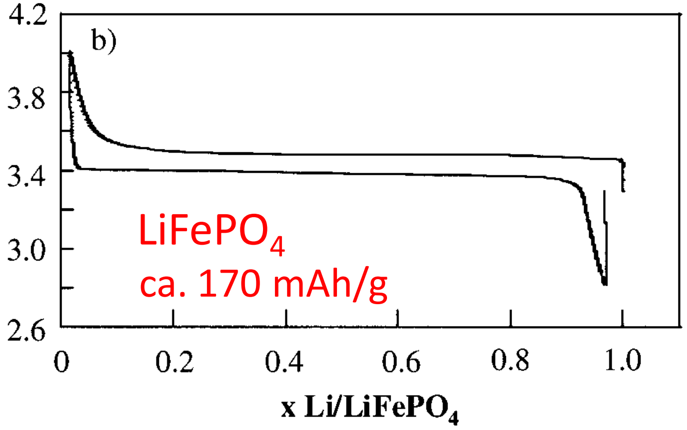
- Change of slope means phase transition
- plateau is a two phase region (Gibbs phase rule) linear slope is one phase region
- Information about polarisation from variation of charge/discharge rates (current)

*Charge rate of 1C means complete charge in 1 hour*
*Charge rate of 0.1C means complete charge in 10 hour*



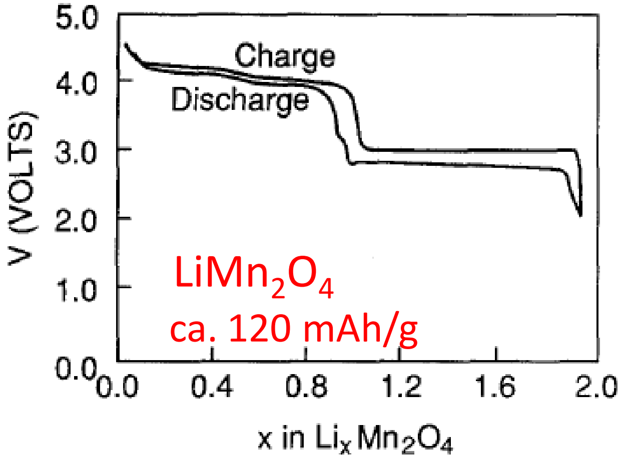
$LiCoO_2$
ca. 140 mAh/g

Carlier et al., J. Electrochem. Soc. 149 (2002) A1310



$LiFePO_4$
ca. 170 mAh/g

*Huang et al., Electrochem. Solid- State Lett., 4 (2001) A170*



$LiMn_2O_4$
ca. 120 mAh/g

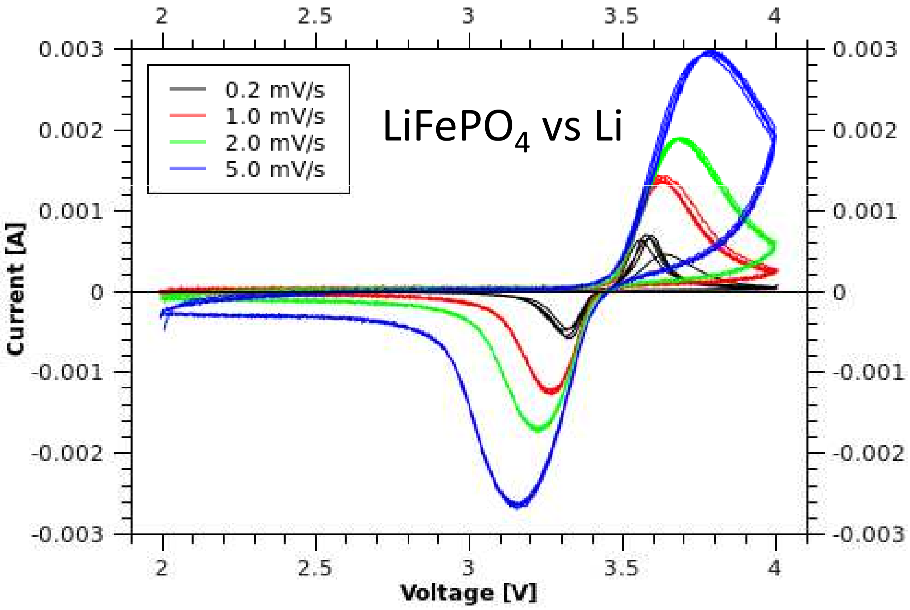
Tarascon et al., J Electrochem. Soc. 138 (1991) 2859

# Electrochemical methods

Cycling voltammetrie

→ Determination of the redox potential and transport properties

Current measurement while sweeping voltage with a defined rate.



$$E_{Li^{+/0}} = -3.04\ \text{V vs. SHE}$$

$$E_{Fe^{3+/2+}} = +0.77\ \text{V vs. SHE}$$

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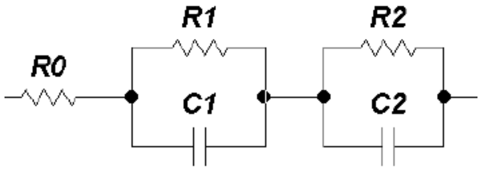
$$\Delta E = 3.81\ \text{V}$$

Difference to experimentally determined 3.4V due to matrix effects (e.g. $PO_4$)

# Electrochemical methods

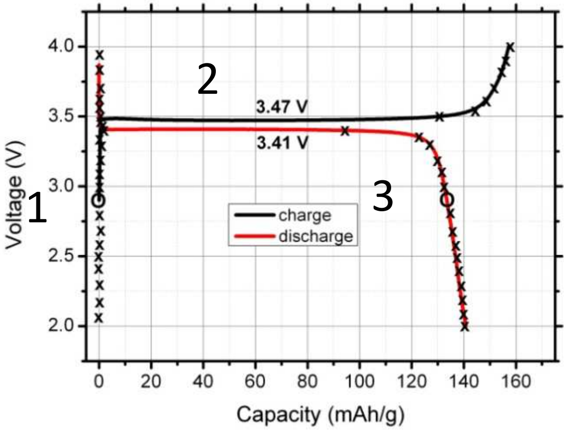
## Impedance spectroscopy

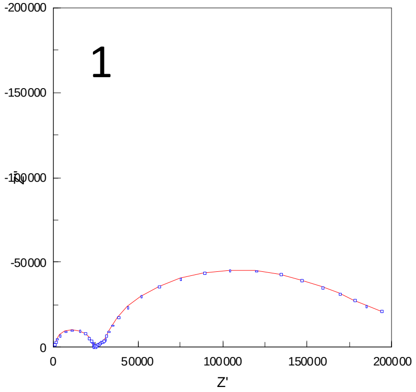


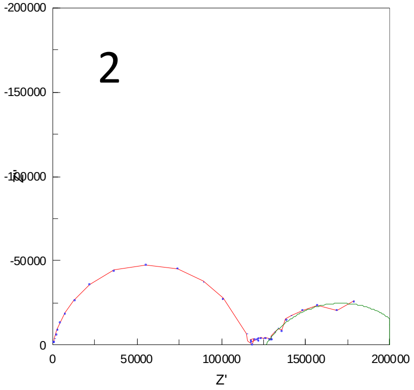
Impedance equivalent circuit

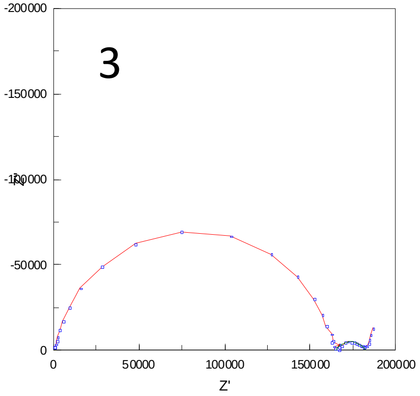
$$Z_R = R$$

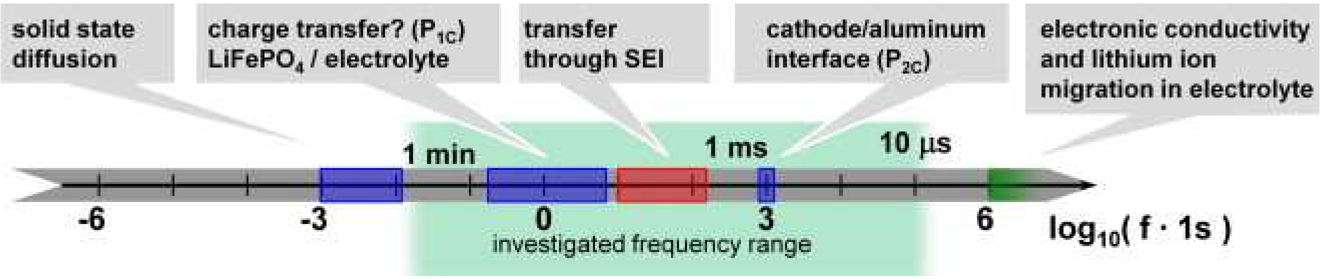
$$Z_C = -j\frac{1}{\omega C}$$











solid state diffusion

charge transfer? ($P_{1C}$) $LiFePO_4$ / electrolyte

transfer through SEI

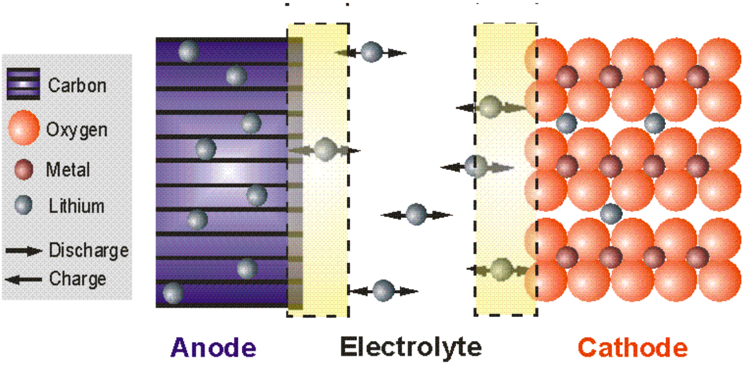
cathode/aluminum interface ($P_{2C}$)

electronic conductivity and lithium ion migration in electrolyte

J. Power Sources 196 (2011) 5342

# Unresolved problems

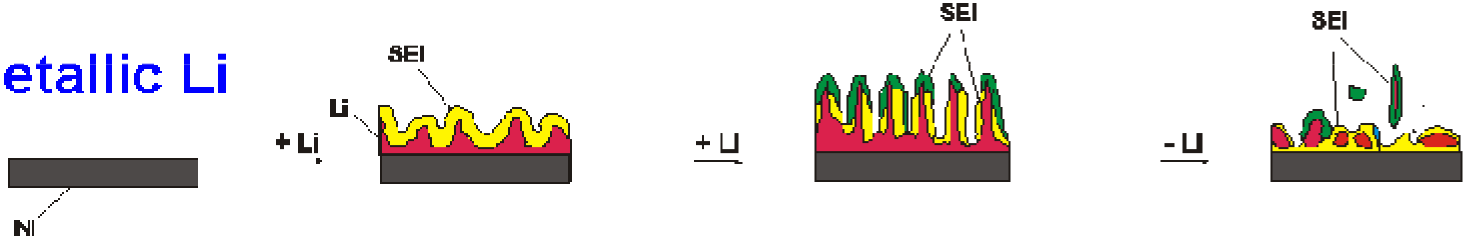
1. Ion transport and intercalation



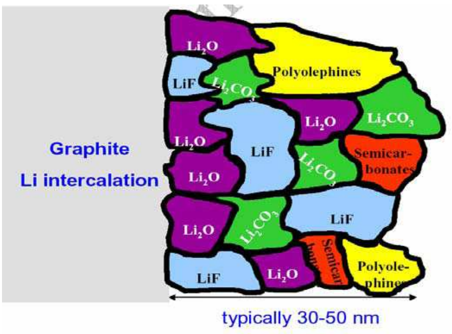
2. Solid-Electrolyte-Interface

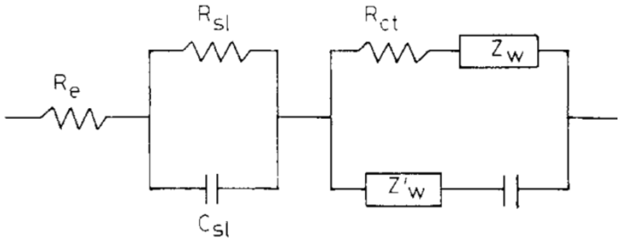
   a) Growth and destruction

**Metallic Li**



   b) Phase composition and transport properties





electrical equivalent cirquit

DOE Report, 2007

# Spectroelectrochemistry

Definition: In situ spectroscopy during electrochemical reaction

Benefits: - follow the dynamic behavior of an electrochemical reaction
- resolve intermediate and metastable products

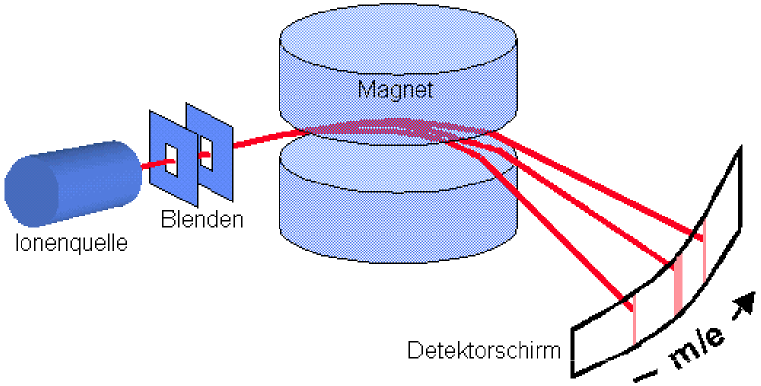
Methods:

- Differential electrochemical mass spectroscopy DEMS
- Ellipsometry
- UV- and visible spectroscopy
- Infrared spectroscopy
- Raman spectroscopy
- X-ray diffraction
- X-ray absorption spectroscopy
- Photoelectron spectroscopy
- Nuclear meagnetic resonance spectroscopy
- Electron spin resonance spectroscopy
- Electron microscopy (EELS)
- . . .

# Differential electrochemical mass spectrometry

## Principle of mass spectrometry

### Single focussing



www.icbm.de/~mbgc/Barni/Image2.gif

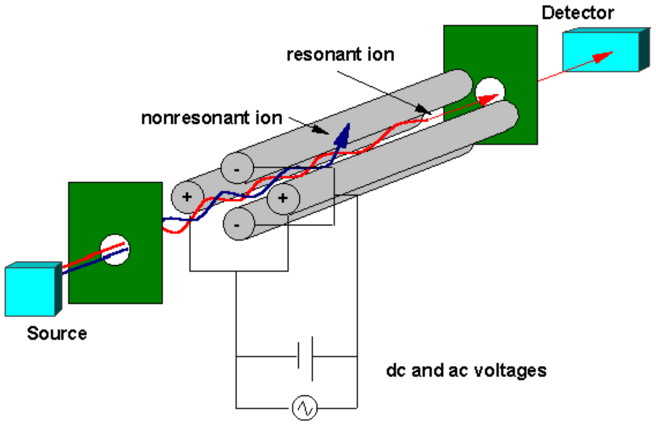
Deflection due to magnetic field

$$F_L = Bev = \frac{mv^2}{R} = F_{ZF}$$

$$E_{kin} = \frac{1}{2}mv^2 = eU = E_{el}$$

$$\Rightarrow R = \frac{1}{B}\sqrt{\frac{m}{e}2U}$$

### Quadropole



www.files.chem.vt.edu/chem-ed/ms/graphics/quad-sch.gif

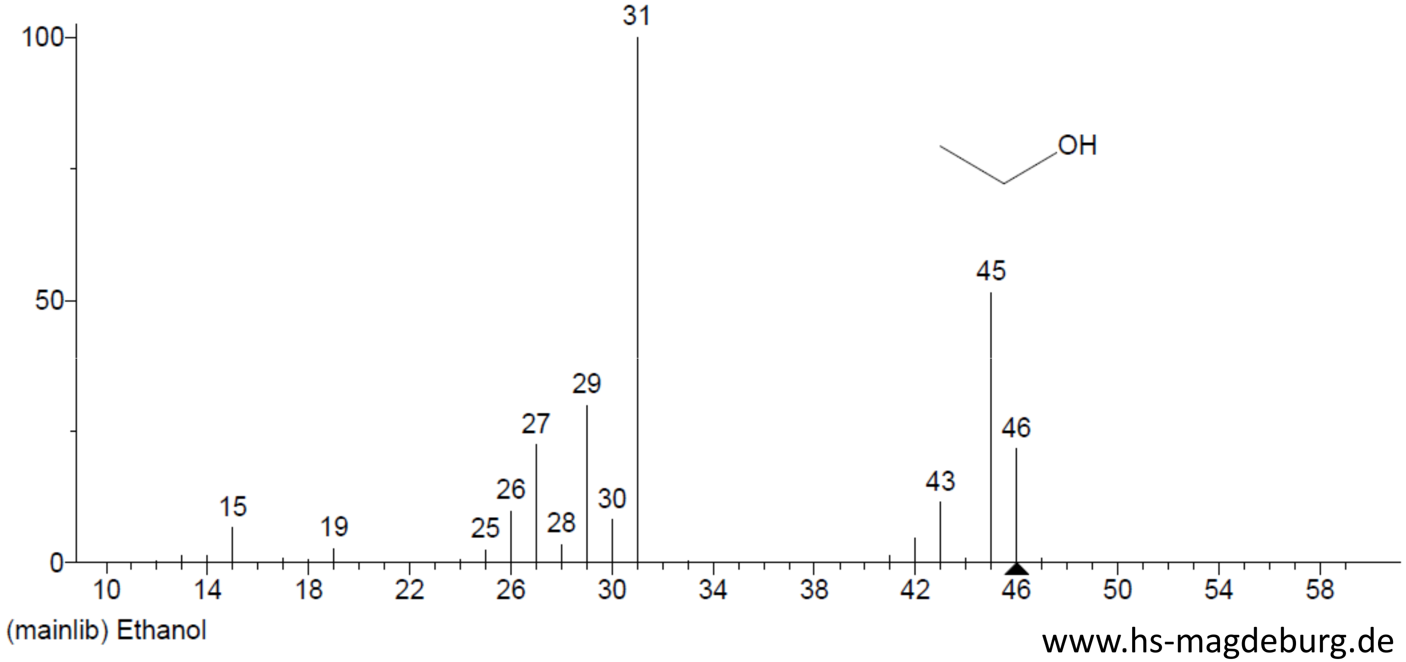
Deflection due to electrical field (DC and AC)

$$U_1 = U_0 + V\cos(2\pi\nu t)$$

$$U_2 = -U_0 - V\cos(2\pi\nu t)$$

# Differential electrochemical mass spectrometry

## Example spectrum (Ethanol)

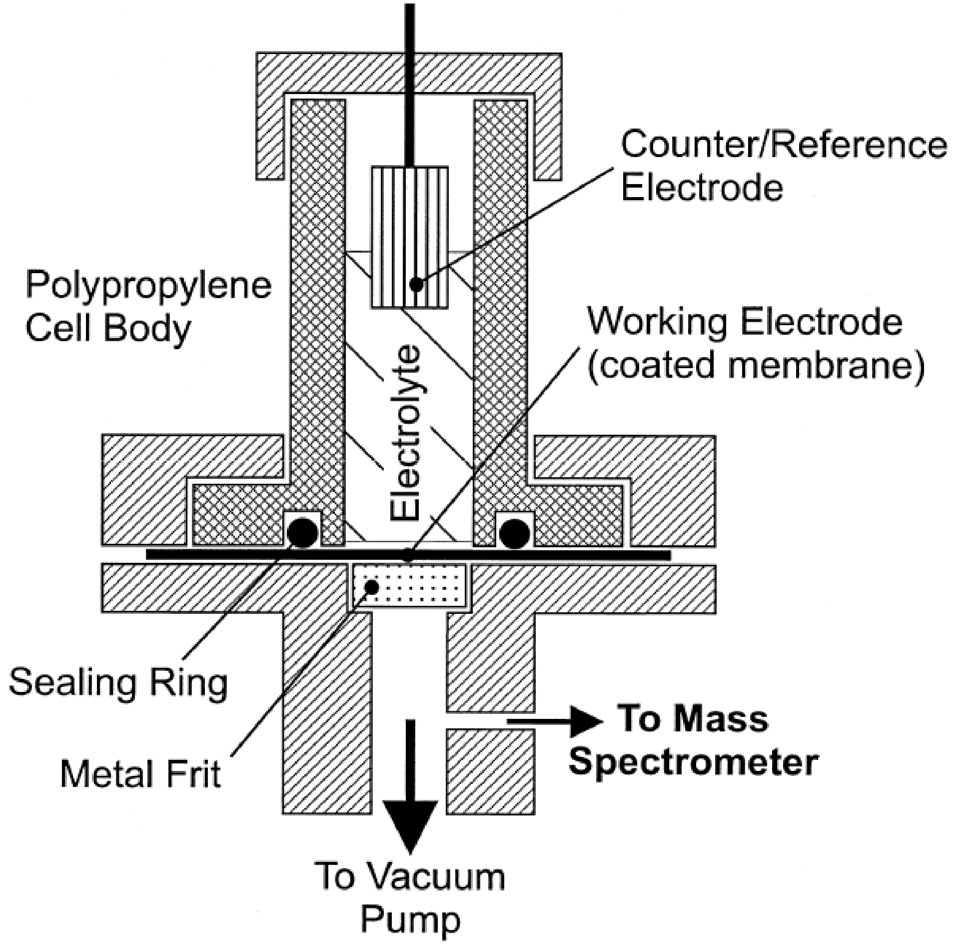


www.hs-magdeburg.de

Decomposition of the molecules due to ionisation

# Differential electrochemical mass spectrometry

In situ cell setup (DEMS)

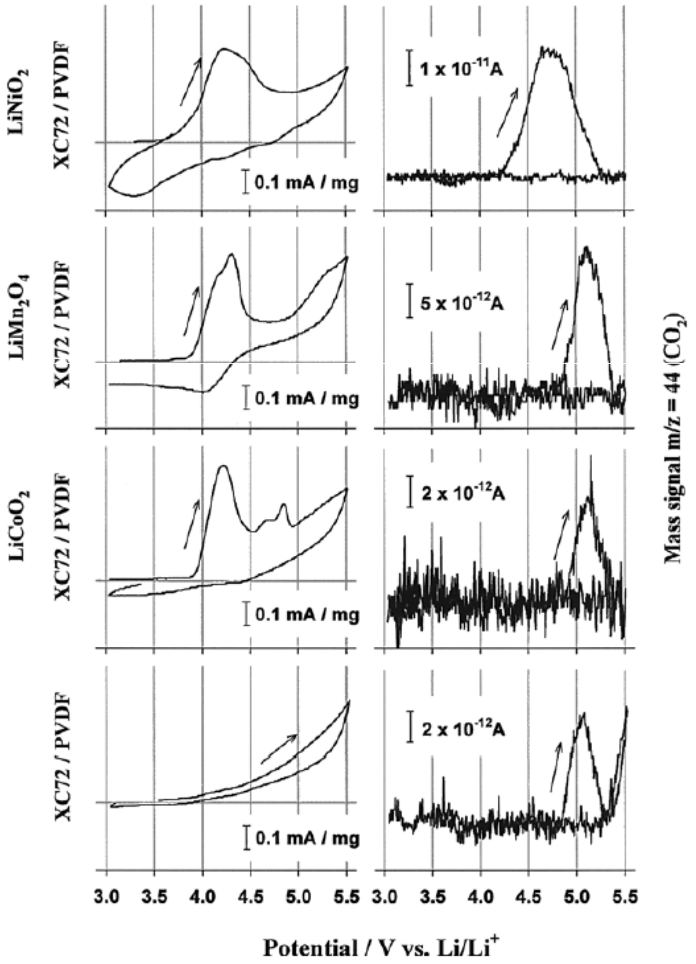


J. Power Sources 90 (2000) 52

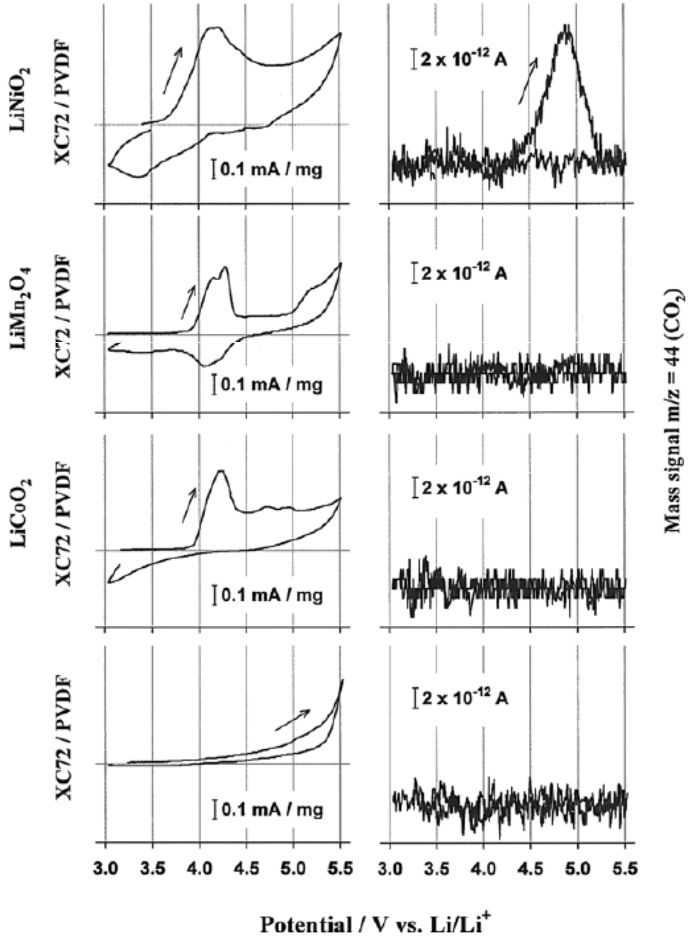
# Differential electrochemical mass spectrometry

DEMS ($CO_2$) on different cathodes and electrolytes

PC



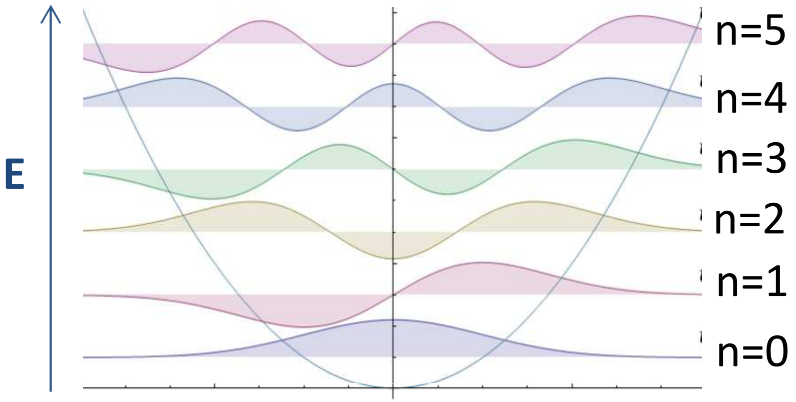
EC/DMC



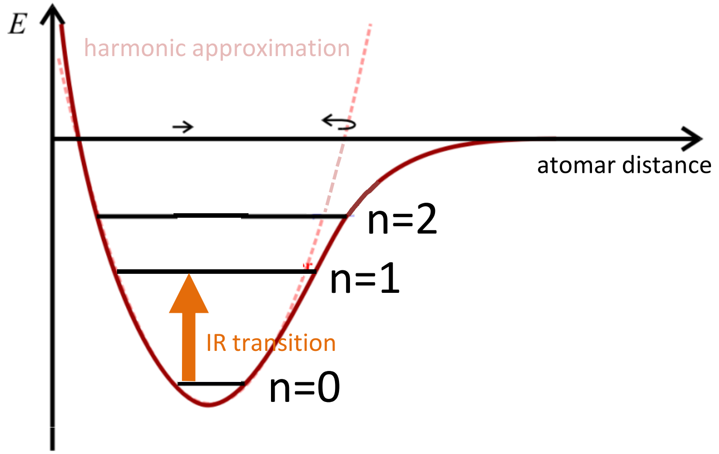
J. Electrochem. Soc. 146 (1999) 1702

# In situ infrared spectroscopy

## Principle of infrared spectroscopy

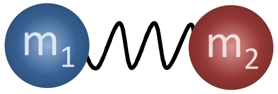

Harmonic oszillator

AllenMcC., HarmOsziFunktionen, Wikimedia Commons



Physical background: Exitation of higher virbrational modes n due to energy absorption

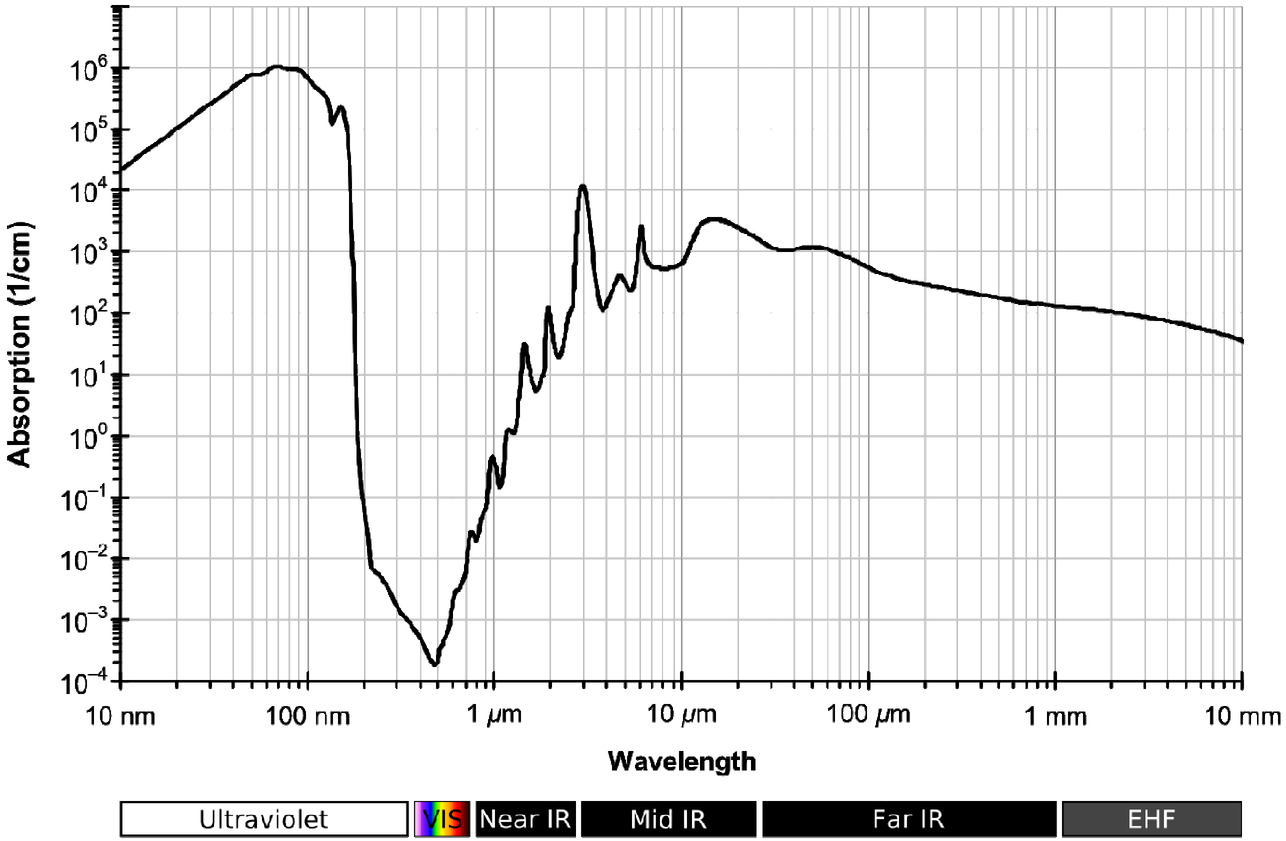
Harmonic oscillator: $\nu_m = \frac{1}{2\pi}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$



quantisized Energy: $E = \left(n+\frac{1}{2}\right)h\nu_m$

# In situ infrared spectroscopy

Infrared absorption in water

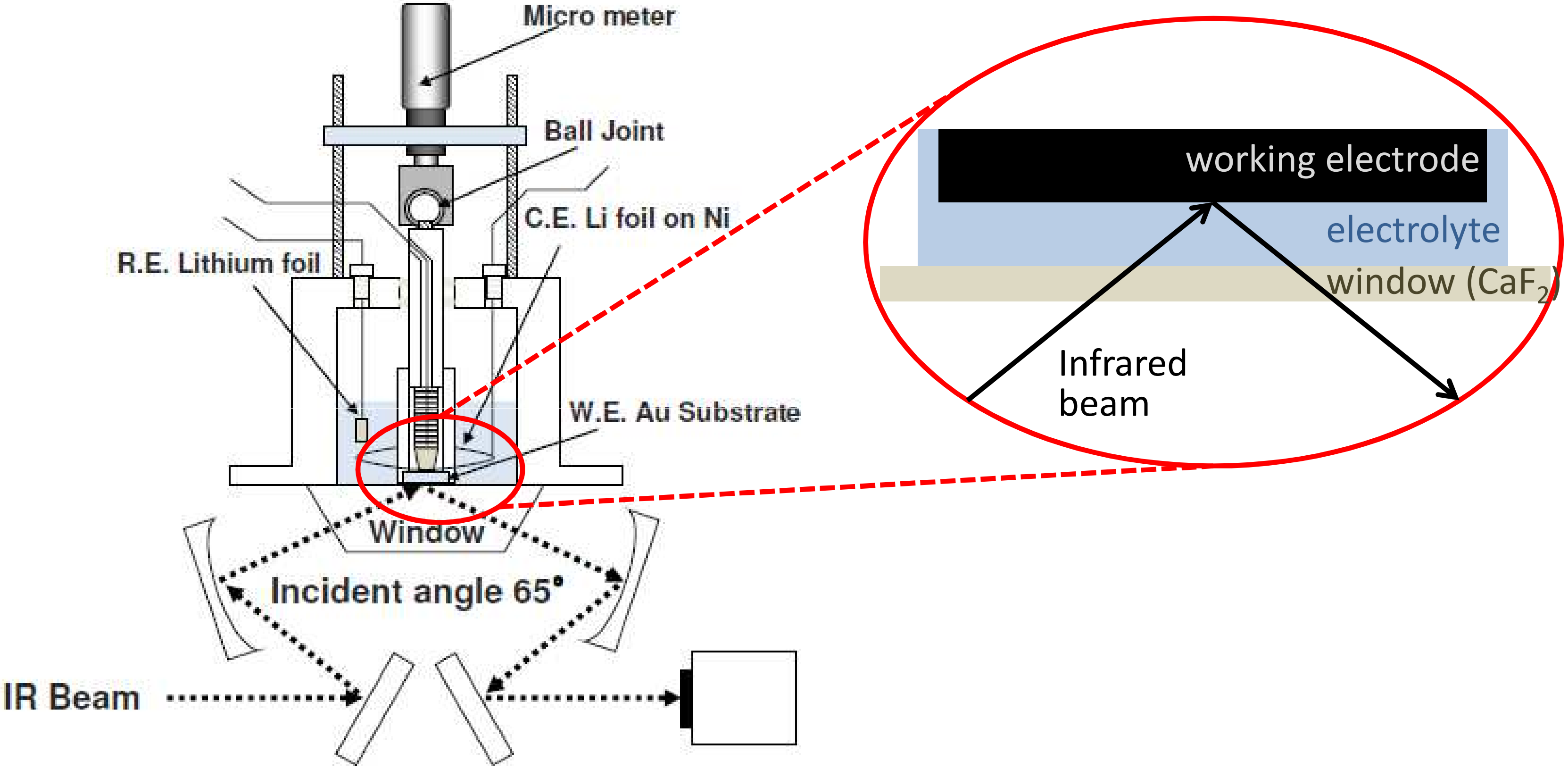


Kebes, Wikimedia Commons

Water (and other polar solvents) absorb IR light → Problem for Spectroelectrochemistry

# In situ infrared spectroscopy

## In situ cell setup (external reflection)

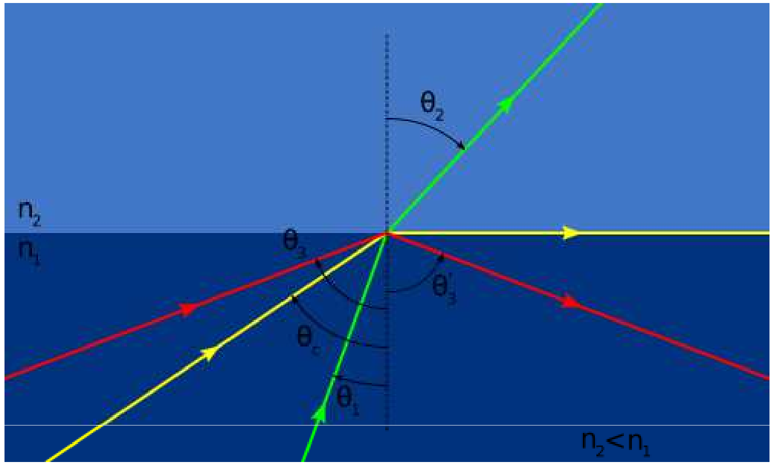


J. Electrochem. Soc. 157 (2010) A121

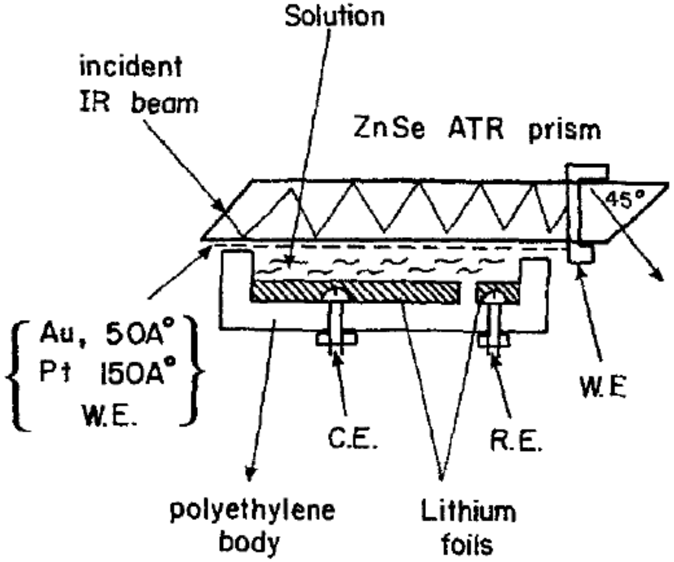
Problems:
- Polar solvents (as typically used in batteries) absorb IR light
- black samples (as typical for battery electrodes) absorb IR light
- large distance between counter and working electrode (significant ohmic drop)

# In situ infrared spectroscopy

## In situ cell setup (attenuated total reflection)



www.geothermie.de/typo3temp/pics/f332292d5e.png



J. Electrochem. Soc. 138 (1991) L6

Snellius law: $\sin(\Theta_{krit}) = \frac{n_2}{n_1}$

Total reflection if $\Theta > \Theta_{krit}$

Penetration depth of evanescent wave:

$$d_{pe} = \frac{\lambda}{2\pi\sqrt{\sin^2(\Theta) - \left(\frac{n_2}{n_1}\right)^2}}$$

Pro

- low absorption in electroyte
- good electrical pathway

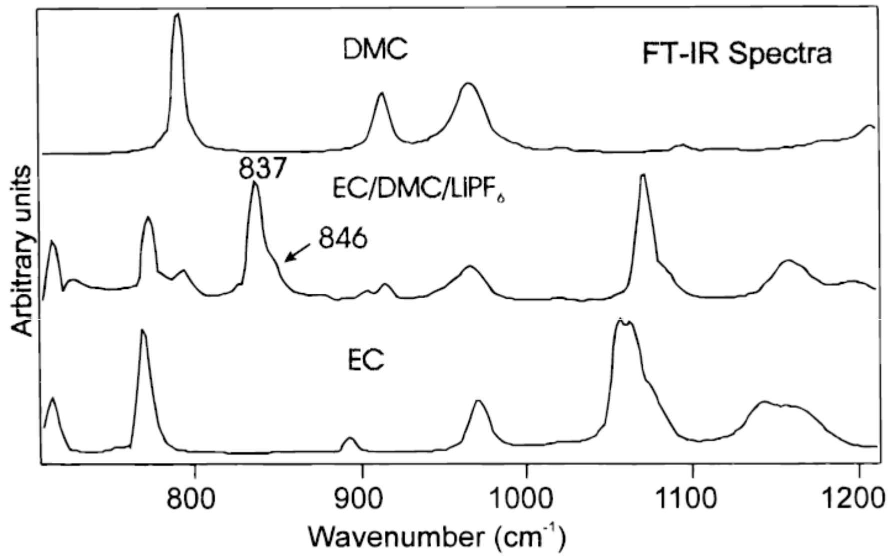
Contra

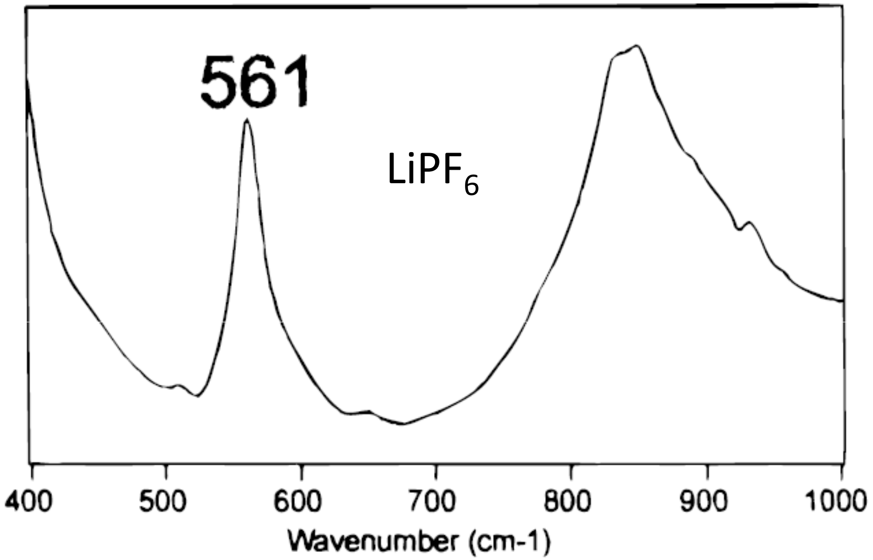
-no active electrode (only thin metal film)

- decomposition of ATR-crystal
  (esp. at low potentials -> anode reaction)

# In situ infrared spectroscopy

Infrared spectrum of typical electrolyte for Li-ion batteries (on ATR-FTIR)

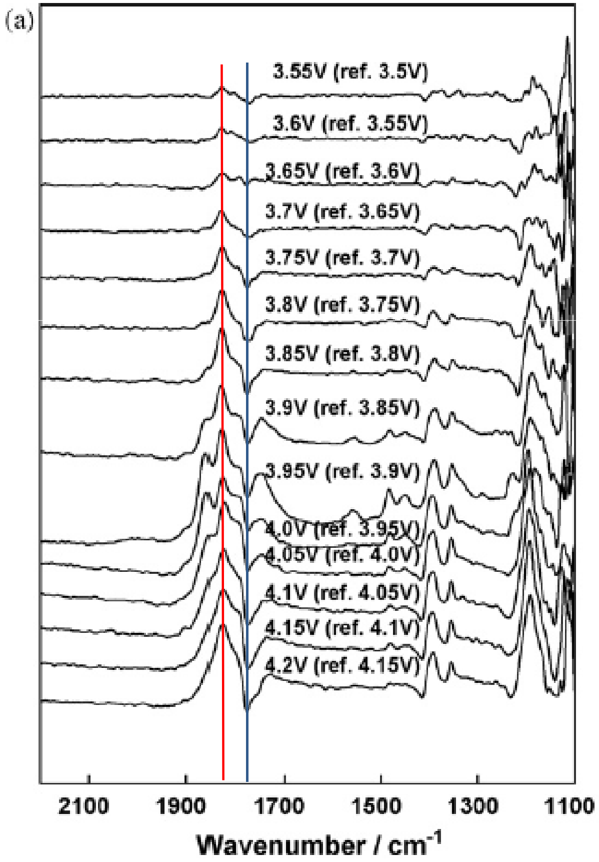




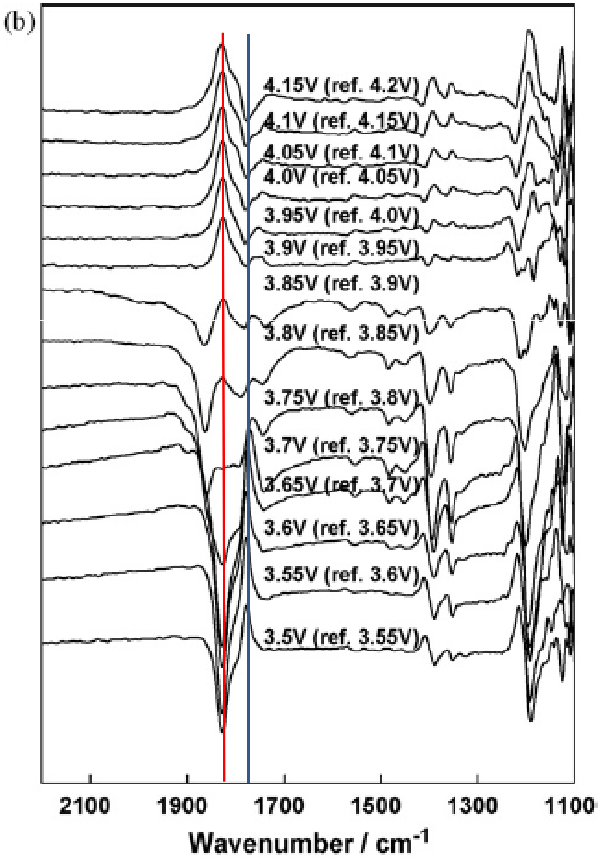
J. Sol. Chem. 29 (2000) 1047

# In situ FTIR (external reflection) for surface film formation on LiCoO2

charge



discharge



J. Power Sources 177 (2008) 184

Peak assignment for *in situ* FTIR spectra for the electrochemical oxidation of propylene carbonate containing 1.0 mol dm$^{-3}$ $LiClO_4$ on the $LiCoO_2$ thin film

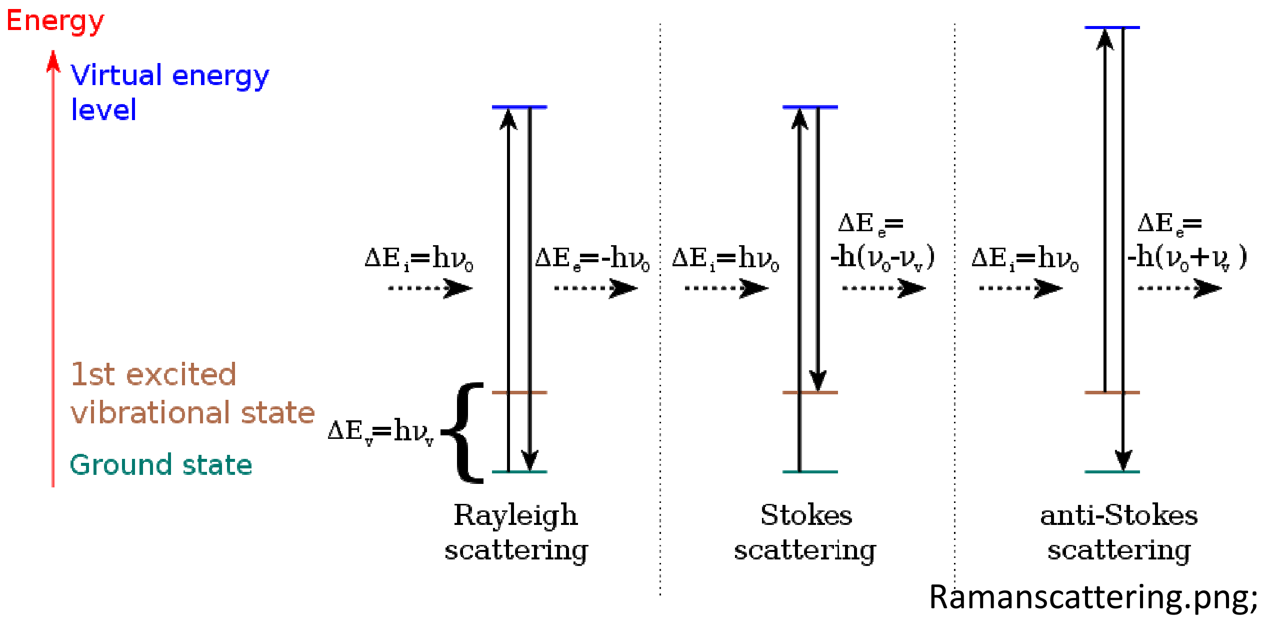
| cm$^{-1}$ | Upward peaks |
|---|---|
| 1830 | C═O stretching vibration in PC |
| 1565 | O–C═O bending vibration in PC |
| 1485 | $CH_2$ wagging vibration in PC |
| 1455 | $CH_3$ asymmetric bending in PC |
| 1395 | O–$CH_2$ wagging vibration in PC |
| 1355 | $CH_3$ symmetric bending vibration in PC |
| 1190 | C–O–C asymmetric stretching vibration in PC |
| | Downward peaks |
| 1780 | C═O symmetric stretching vibration in decomposition products |
| 1420 | $CH_2$ bending or $CO_2$ symmetric stretching vibration in decomposition products |
| 1375 | $CH_3$ symmetric bending vibration in decomposition products |
| 1235 | C–O–C asymmetric stretching vibration in decomposition products |

Differential spectra:
Positive band: species decrease
Negative peak: species increase

→ reversible surface film formation

# In situ Raman spectroscopy

## Principle of Raman spectroscopy



Ramanscattering.png; Wikimedia Commons

**Physical background:** Change in polarization due to vibration

Incident light: $E = E_0 \cdot \cos(2\pi \cdot \nu_{in} \cdot t)$

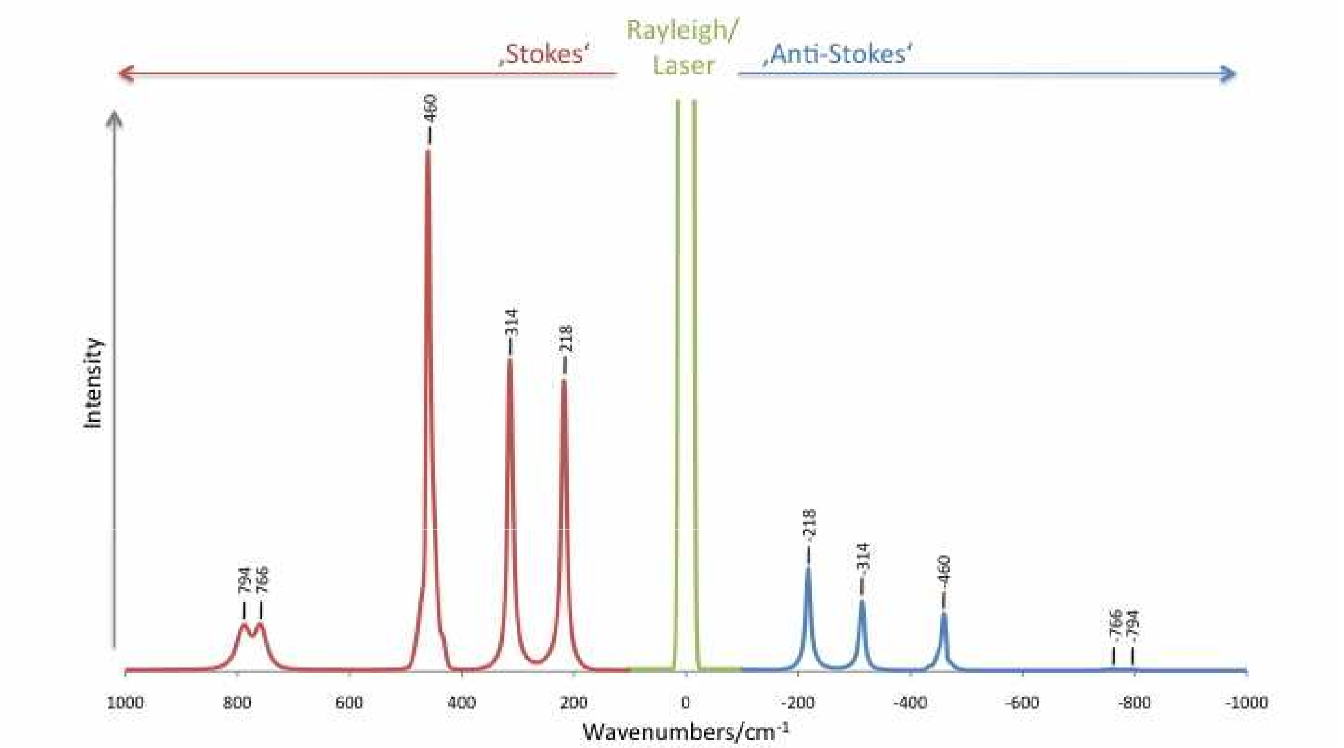
Vibration: $\mathrm{R} = \mathrm{R}_0 + \mathrm{A} \cdot \cos(2\pi \nu_{\mathrm{vib}} \mathrm{t})$

Polarisation: $P = \alpha E$

Polarizabilty: $\alpha(\mathrm{R}) = \alpha(\mathrm{R}_0) + \frac{d\alpha}{dR} \cdot (R - R_0)$

$$P = \underbrace{\alpha(\mathrm{R}_0)\mathrm{E}_0 \cos(2\pi\nu_{\mathrm{in}}\mathrm{t})}_{\textbf{Rayleigh}} + \frac{1}{2}\mathrm{AE}_0 \frac{d\alpha}{dR} \{\underbrace{\cos[2\pi(\nu_{in} - \nu_{\mathrm{vib}})\mathrm{t}]}_{\textbf{Stokes}} + \underbrace{\cos[2\pi(\nu_{in} + \nu_{\mathrm{vib}})\mathrm{t}]}_{\textbf{Anti-Stokes}}\}$$

# In situ Raman spectroscopy



http://www.raman.de/htmlEN/basics/intensityEng.html

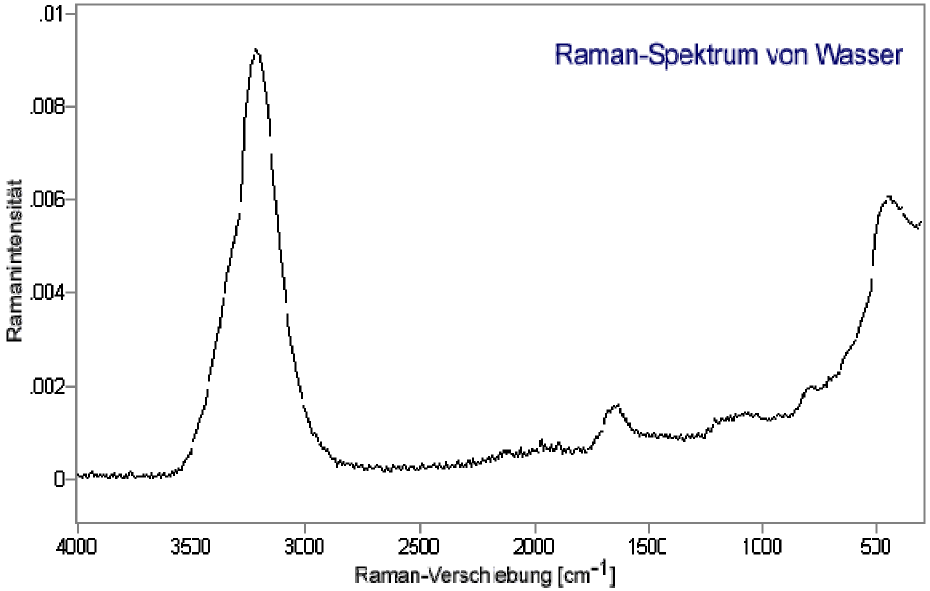
## Intensities

Stokes: $N_0 \rightarrow N_1$
Ant-Stokes: $N_1 \rightarrow N_0$
$N_0$: ground state
$N_1$: first exited state

$$\frac{N_1}{N_0} \propto e^{-\left(\frac{\hbar \nu_{vib}}{kT}\right)}$$

# In situ Raman spectroscopy

Example spectrum (water)

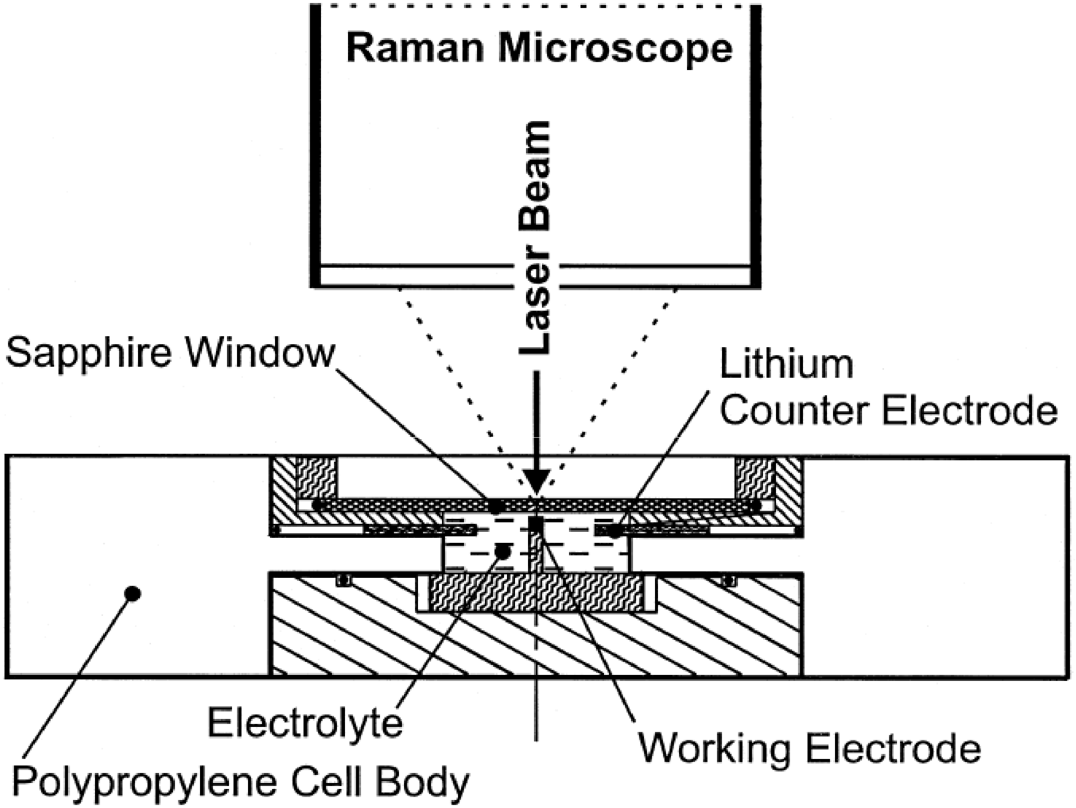


www.chemgapedia.de/vsengine/media/vsc/de/ch/3/anc/ir_spek/raman_spektroskopie/ra_probenvorbereitung/rawasser_m13bi0603.gif

Weak signal from water (and other polar solvents) → no problem for spectrolectrochemistry

# In situ Raman spectroscopy

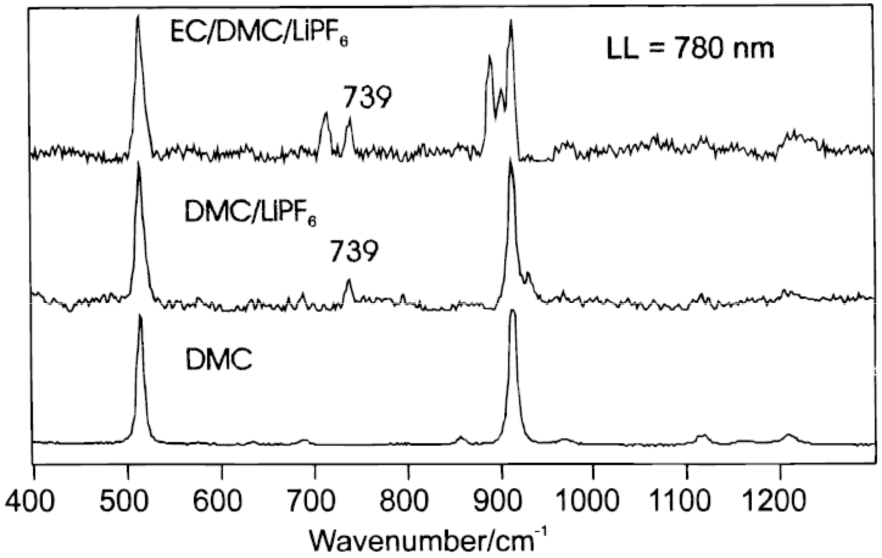
## In situ cell setup

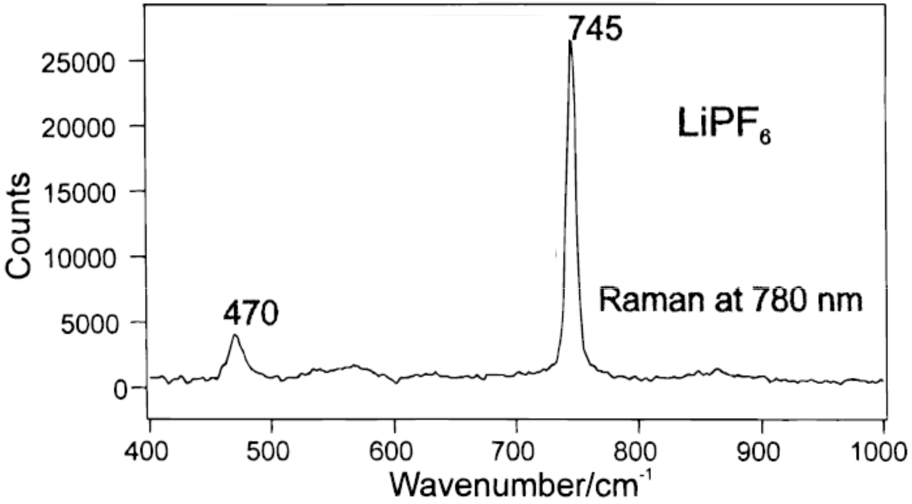


J. Power Sources 90 (2000) 52

# In situ Raman spectroscopy

Raman spectrum of typical electrolyte for Li-ion batteries

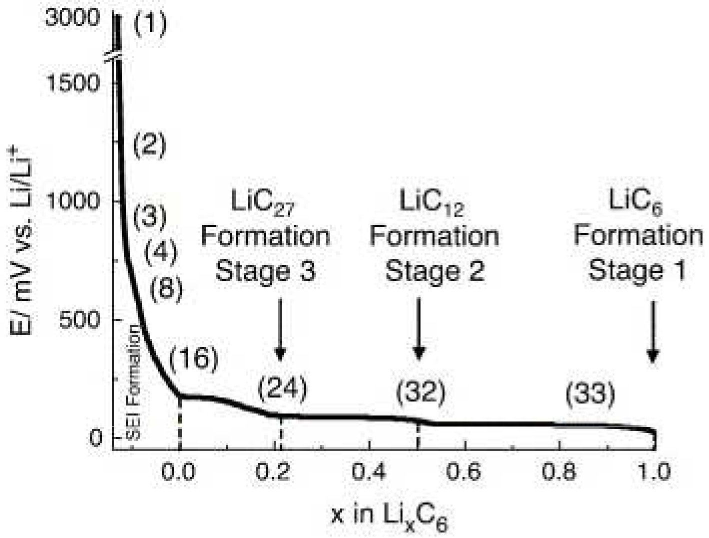




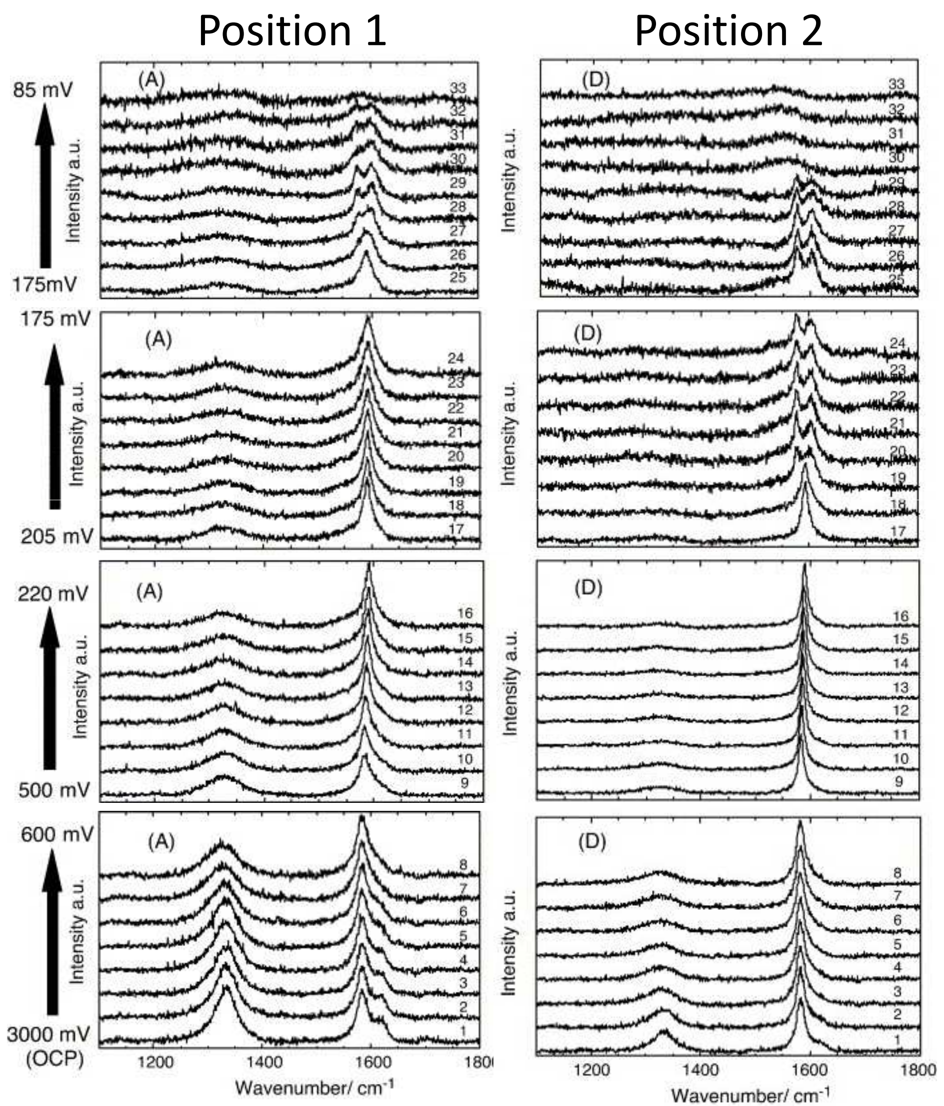
J. Sol. Chem. 29 (2000) 1047

# In situ Raman spectroscopy

In situ Raman on graphite electrode



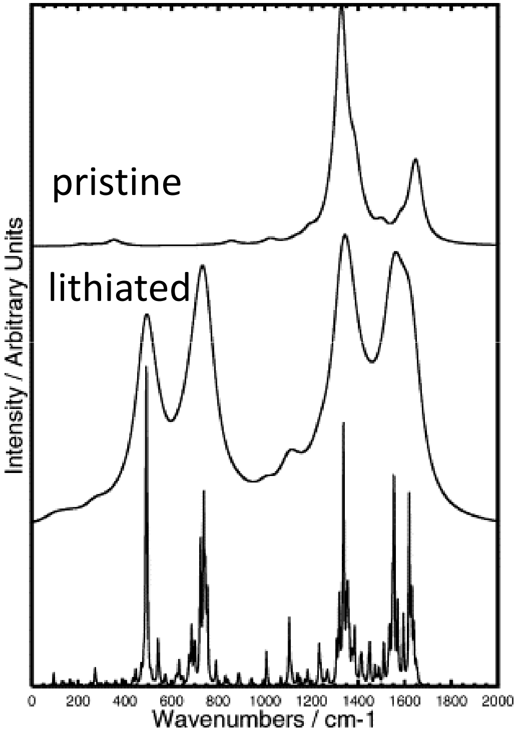
- Inhomogeneities in the sample
- Increase of $I_G/I_D$ with lower potential
- Phase transition in different states of charge can be observed
- Detailed structure analysis is lacking



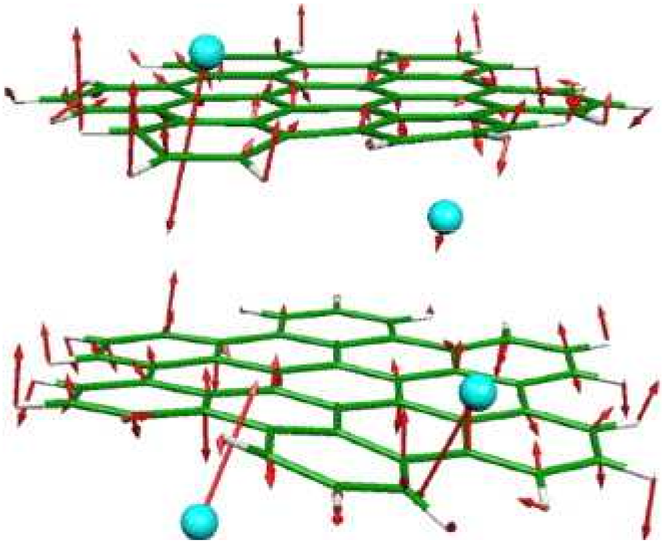
Solid State Ionics 177 (2006) 2801

# In situ Raman spectroscopy

Theoretical Raman spectra of intercalated lithium in amorphous carbon



Vibrations in lithiated carbon

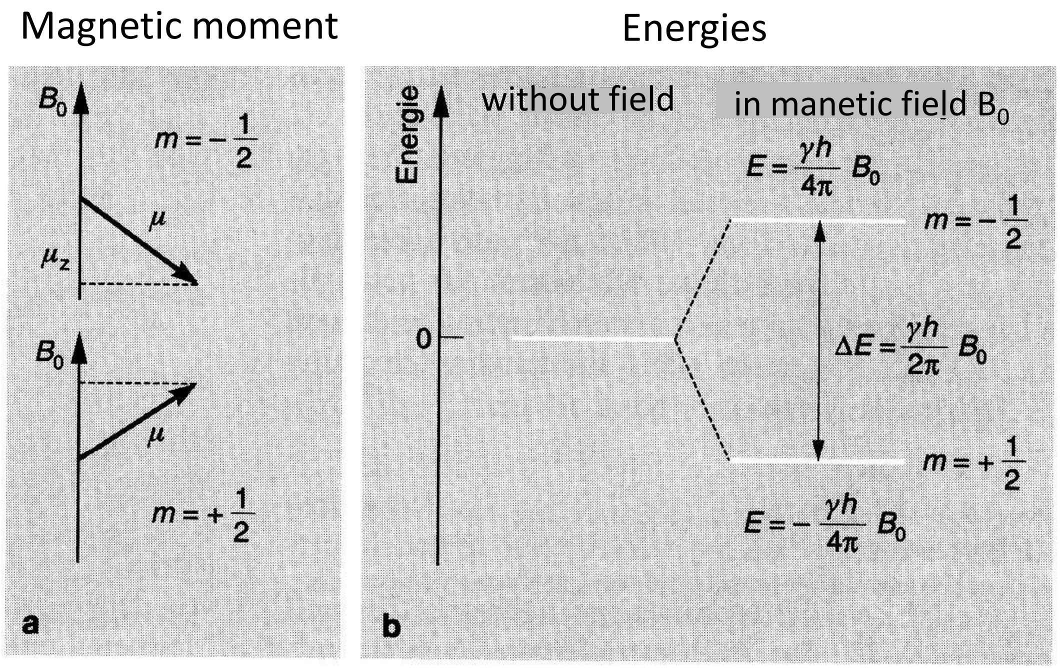


Carbon 42 (2004) 1001

Li-C interaction leads to rise of $I_G/I_D$ and fomation of Li-C band

# In situ nuclear magnetic resonance

Principle of NMR


Magnetic moment

Energies

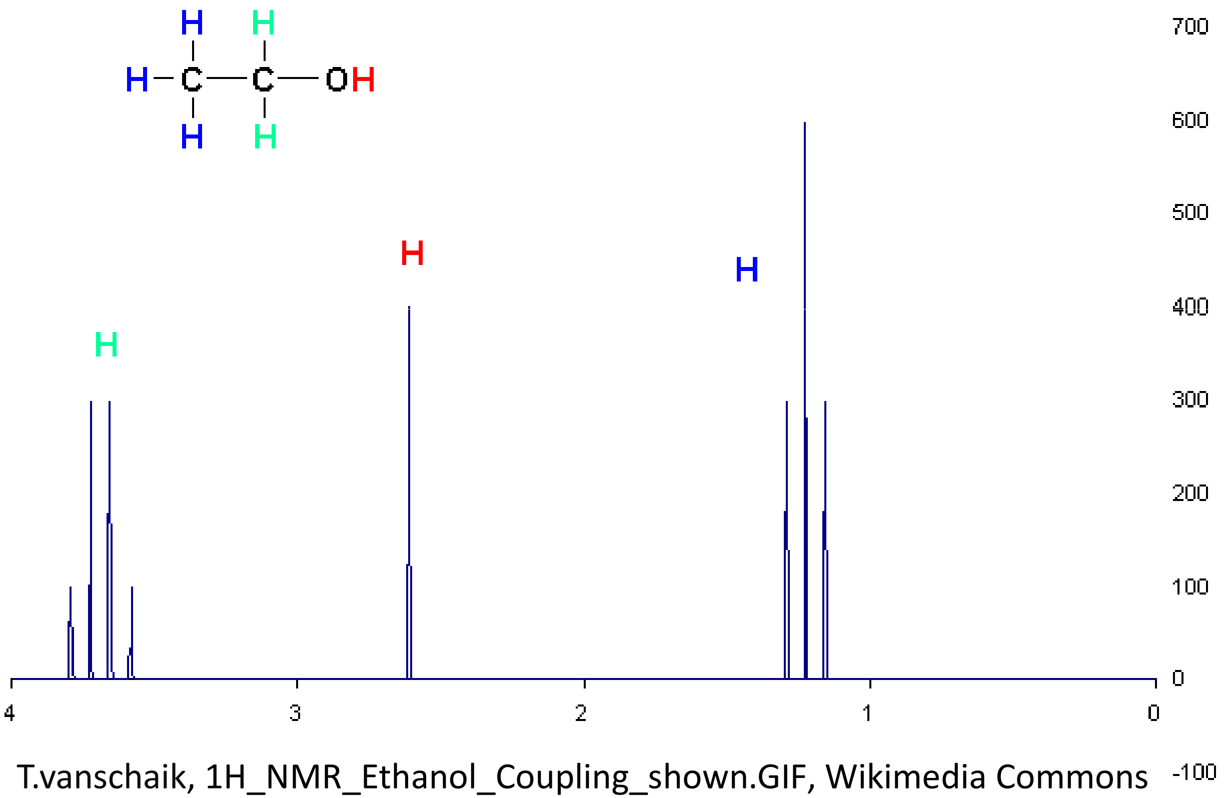
Skoog, Leary; Instrumentelle Analytik; Springer 1996; p. 337

Physical background: Orientation of the core spin induced magnetic moment due to EM-wave absorption

Chemical shift: from electrons induced magnetic field (Lenz rule) shifts effective B and therefore the absorption Energy

Spin-spin coulping: effect of core spins from neighboring cores

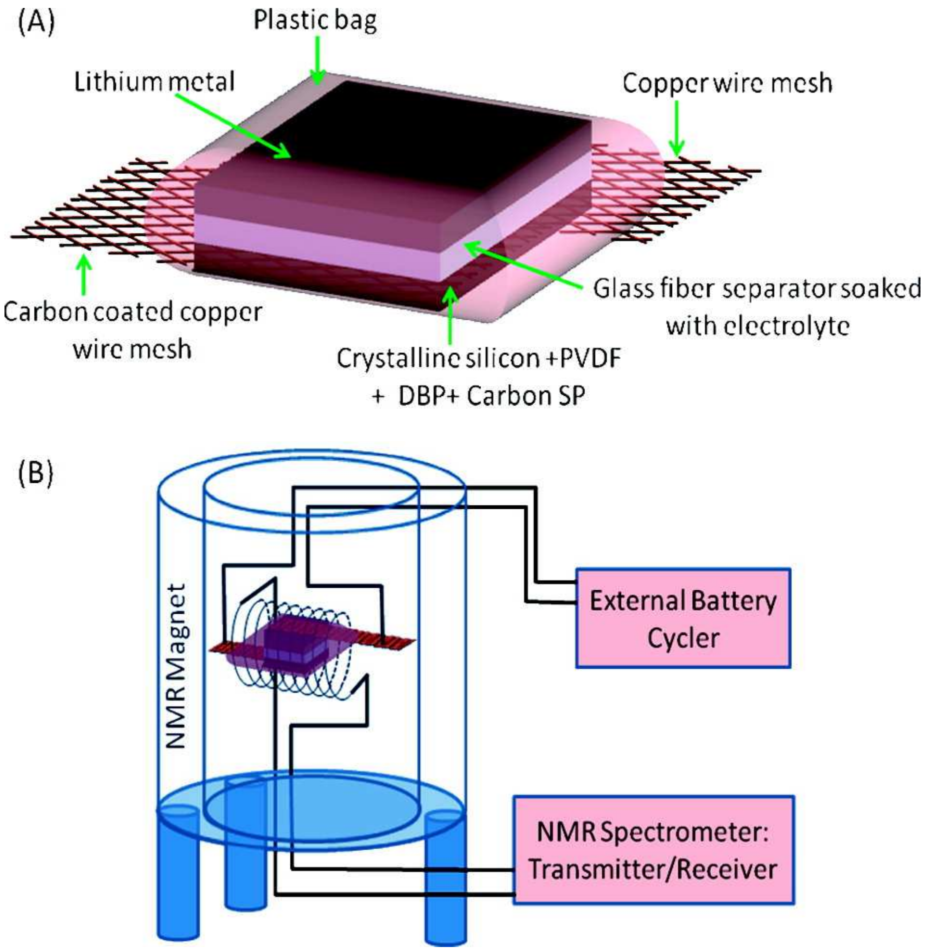
## Example spectrum (ethanol)



T.vanschaik, 1H_NMR_Ethanol_Coupling_shown.GIF, Wikimedia Commons

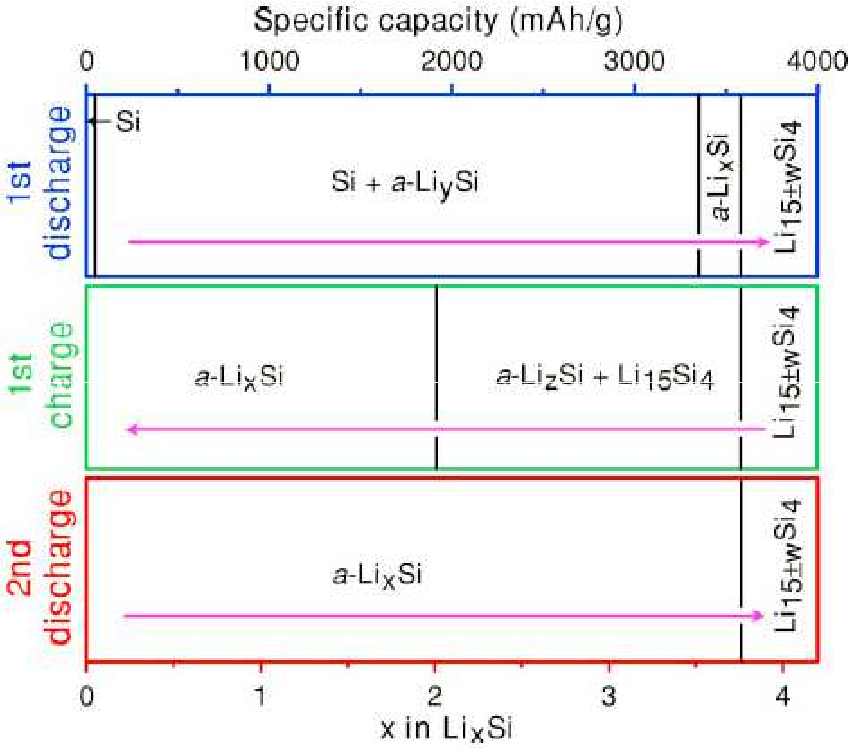
# In situ nuclear magnetic resonance

In situ cell setup



J. Am. Chem. Soc. 131 (2009) 9239

Si anode (in situ XRD)



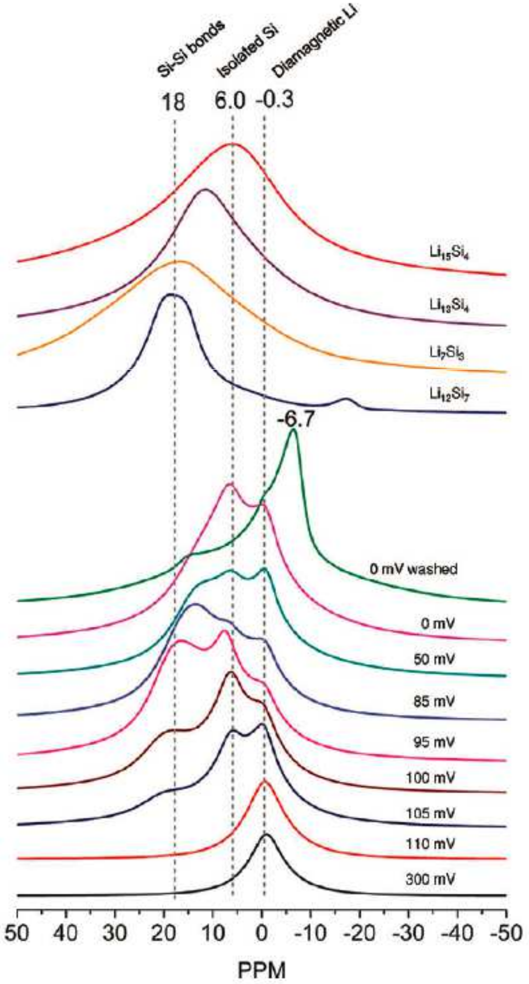
J. Electrochem. Soc. 154 (2007) A156

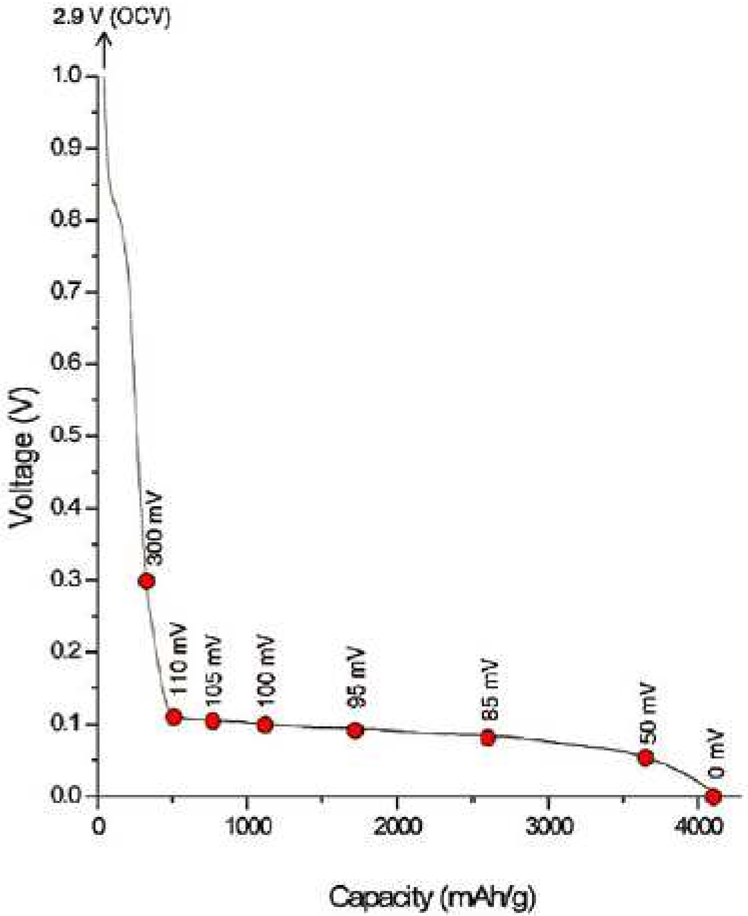
No specific information about amorpgous phase accesible with XRD → use NMR

# In situ nuclear magnetic resonance

## Si anode (ex situ)

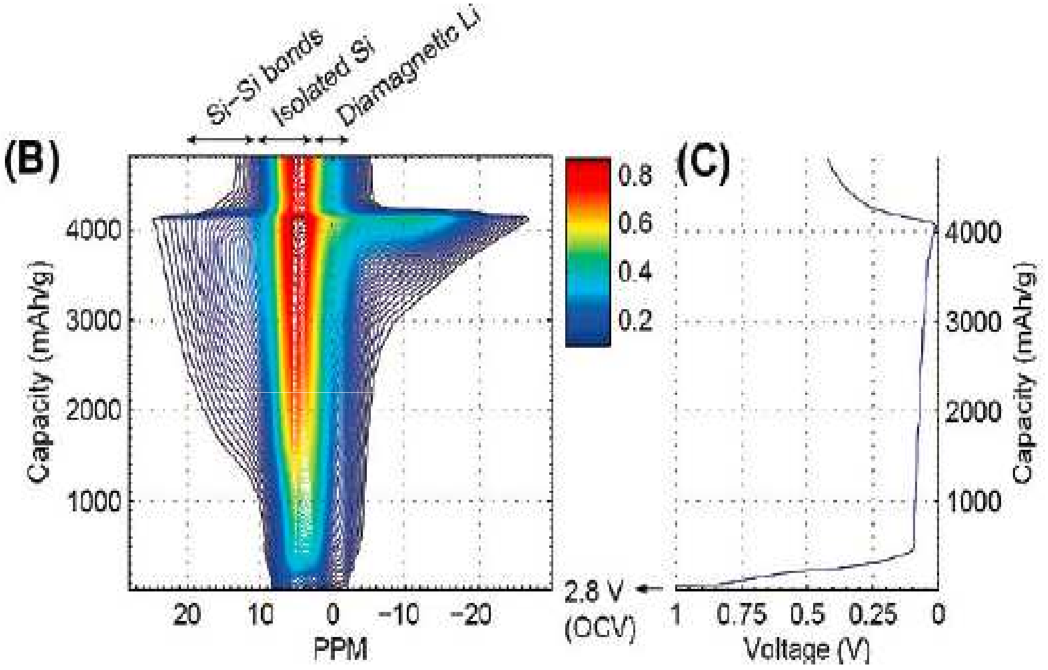
$^7$Li MAS NMR on electrodes after disassembling at different states of charge

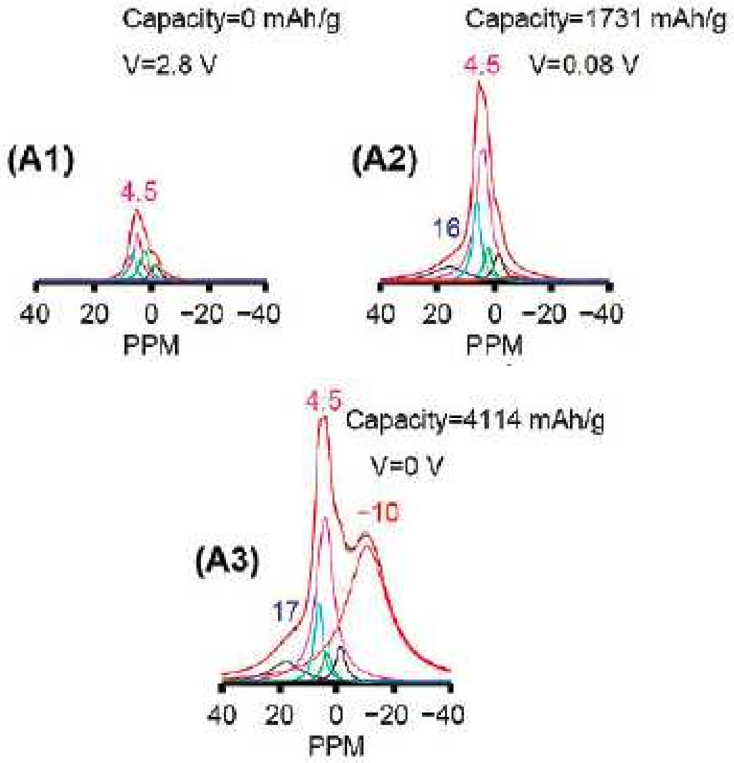




J. Am. Chem. Soc. 131 (2009) 9239

# <u>Si anode (in situ)</u> Static $^7$Li NMR



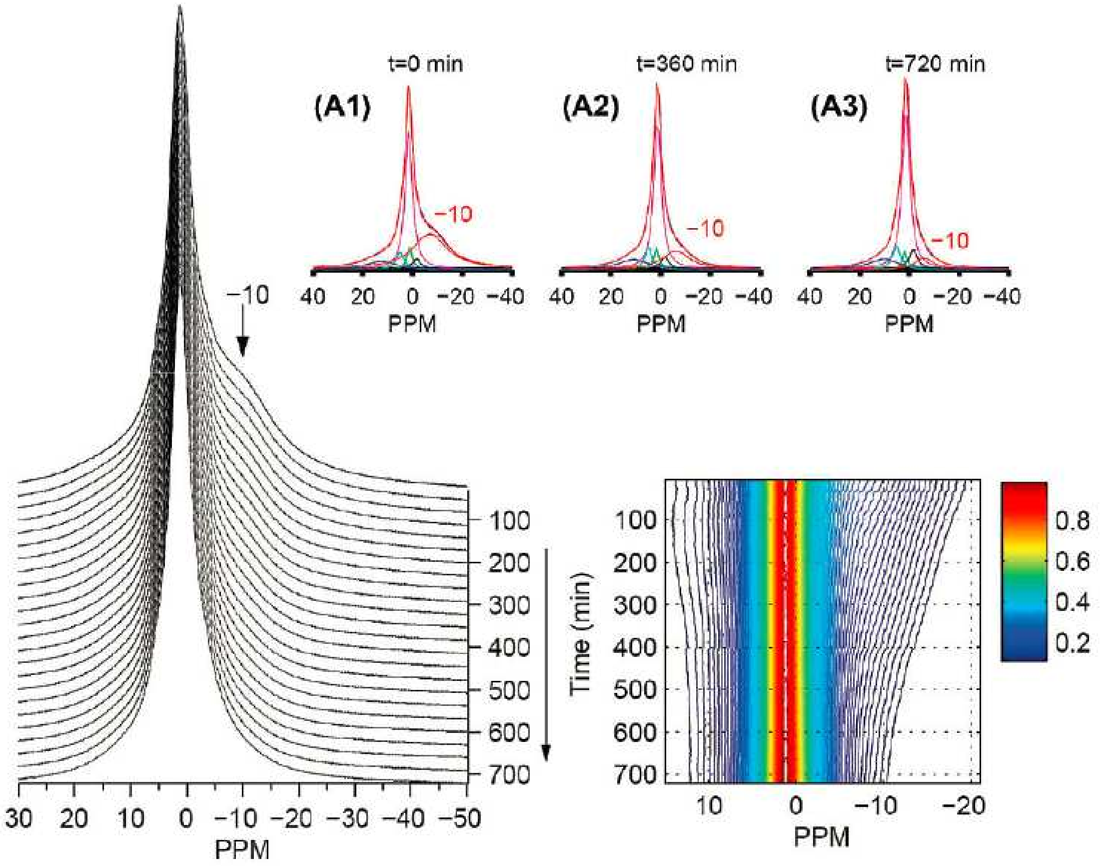


J. Am. Chem. Soc. 131 (2009) 9239

Additional peak forms at -10 ppm, which has not been detected with ex situ NMR

## Si anode (in situ)

Time resolved relaxation after full lithiation (0mV)



→ Self discharge process of the metastable $Li_{15}Si_4$ Phase with the electrolyte.