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Studies of Interfacial Processes of Lithium-Ion Batteries by using In Situ MFTIRS and EQCM

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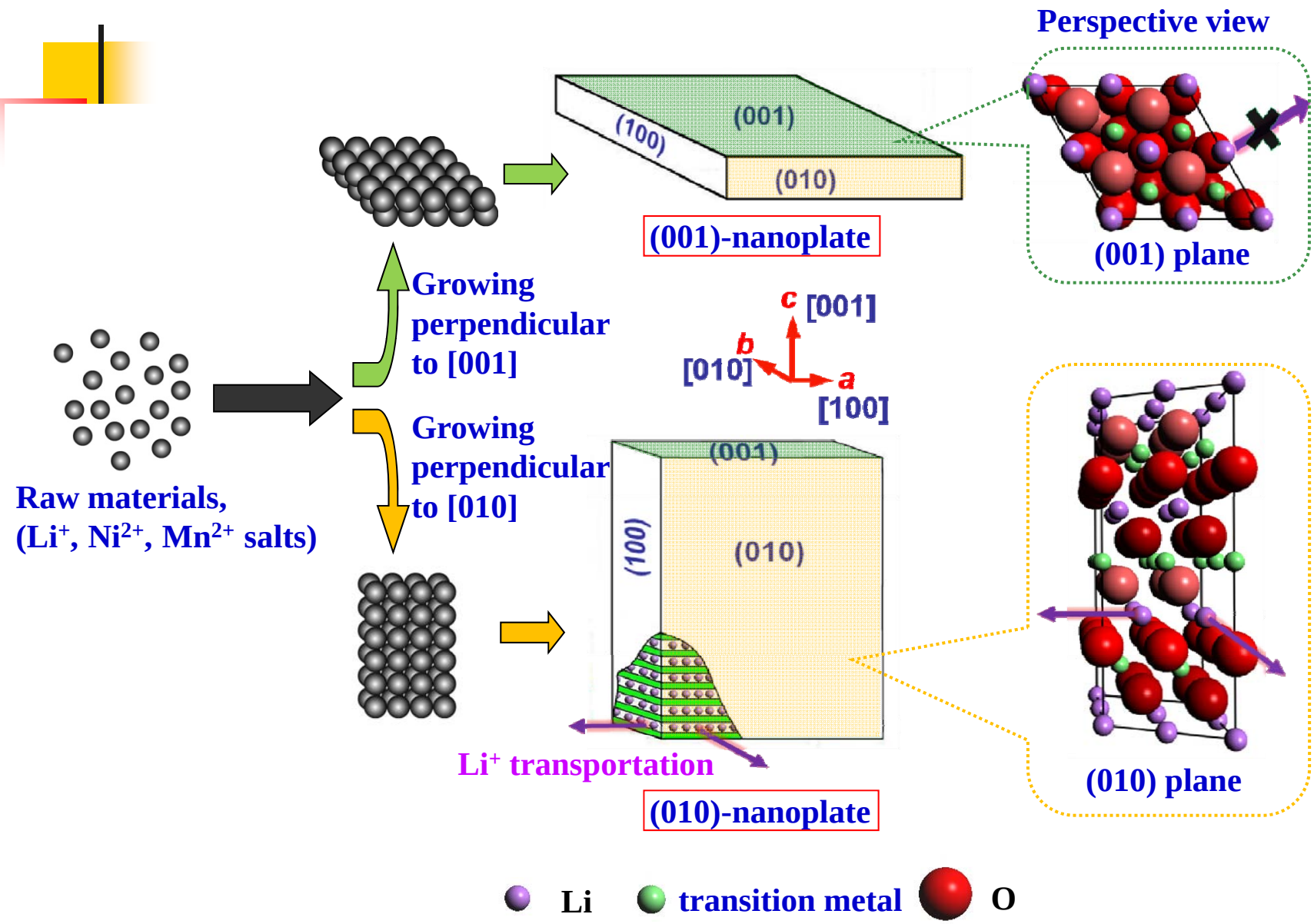
The main studies of EC-power sources in Xiamen University

- Lithium ion batteries
  - 3D nanostructured anode materials
  - Surface structure and property of cathode materials
- High power EC-energy system
- In situ studies of interfacial processes

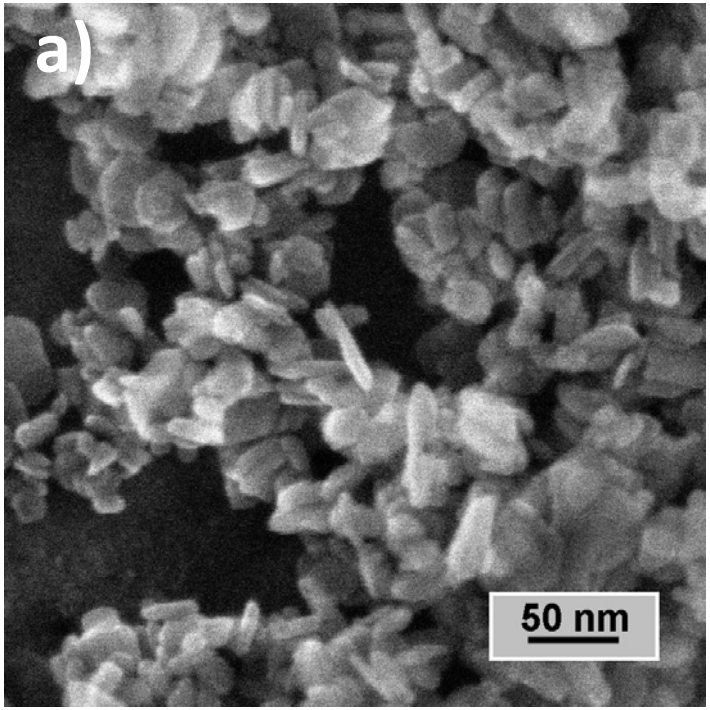
LNMO nanoplates and their surface structure

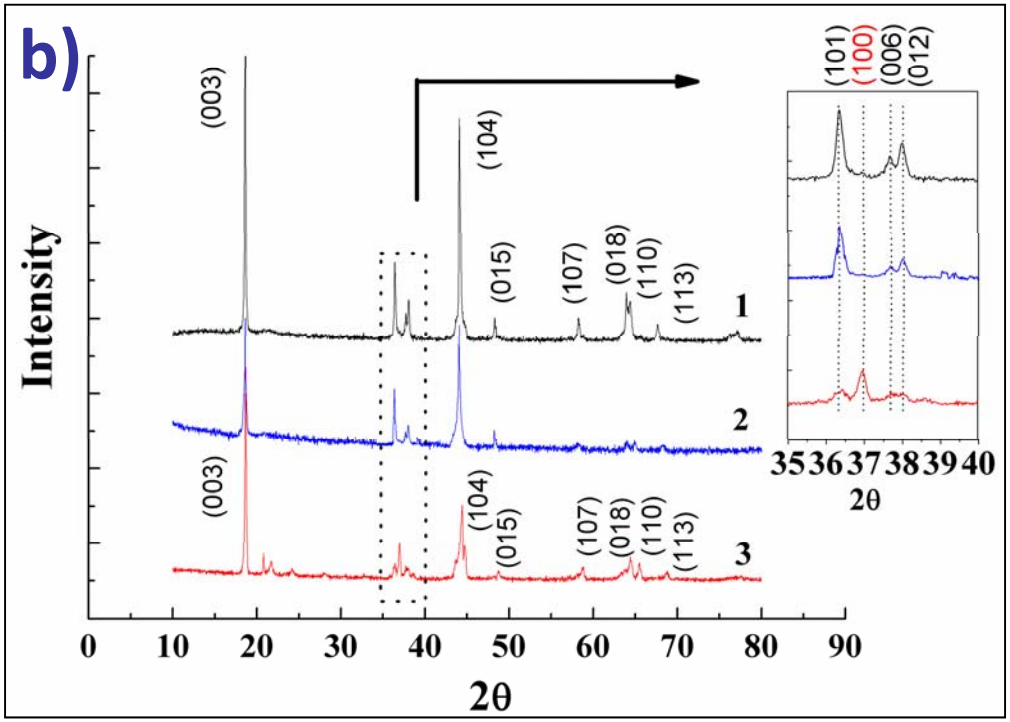


$Li[Li_{1/3-2x/3}Ni_xMn_{2/3-x/3}]O_2$

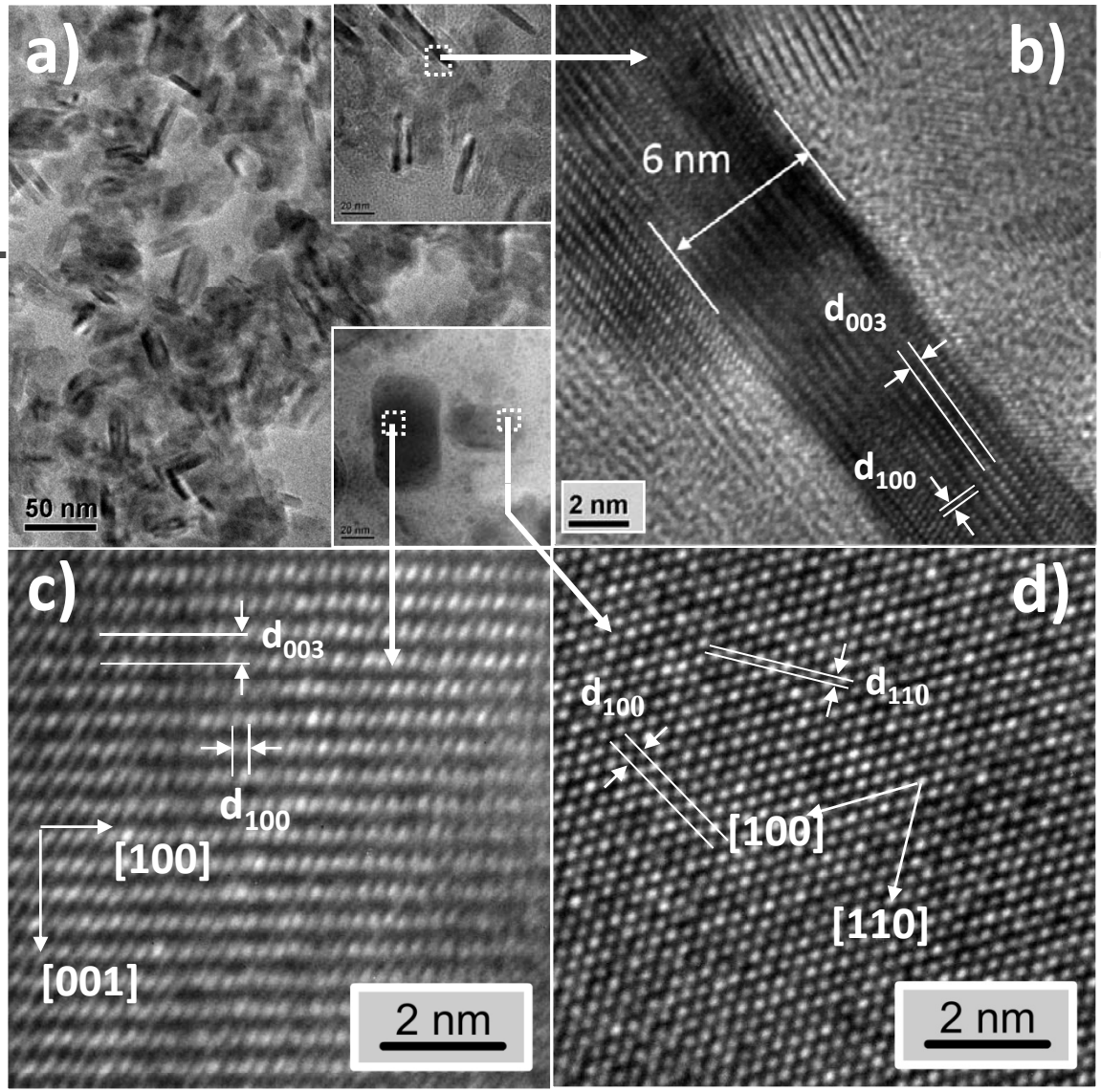
1. Particles
2. Conventional nanoplates (CN)
3. Habit-tuned nanoplates (HTN)

HTN





SEM & XRD



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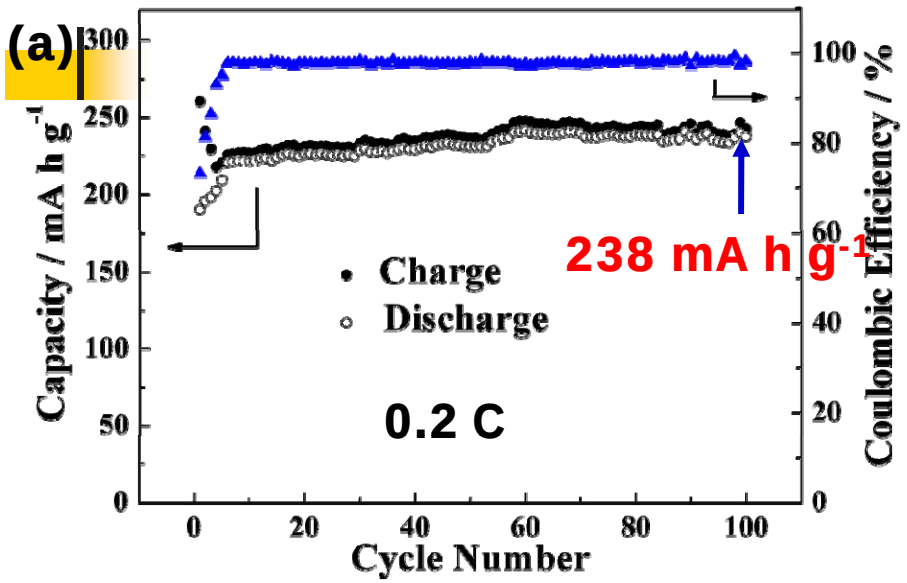
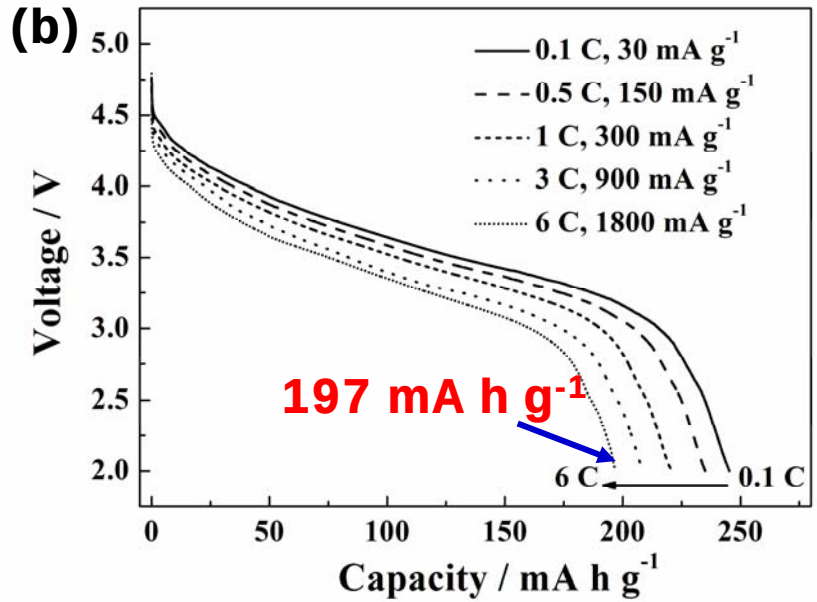
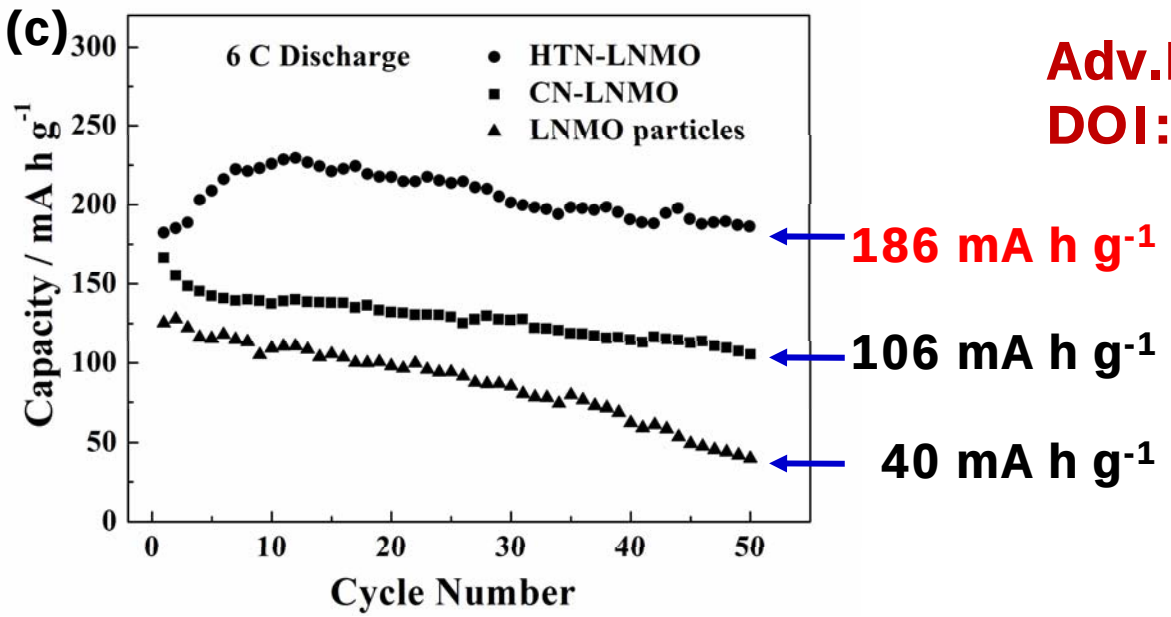
TEM Characterization







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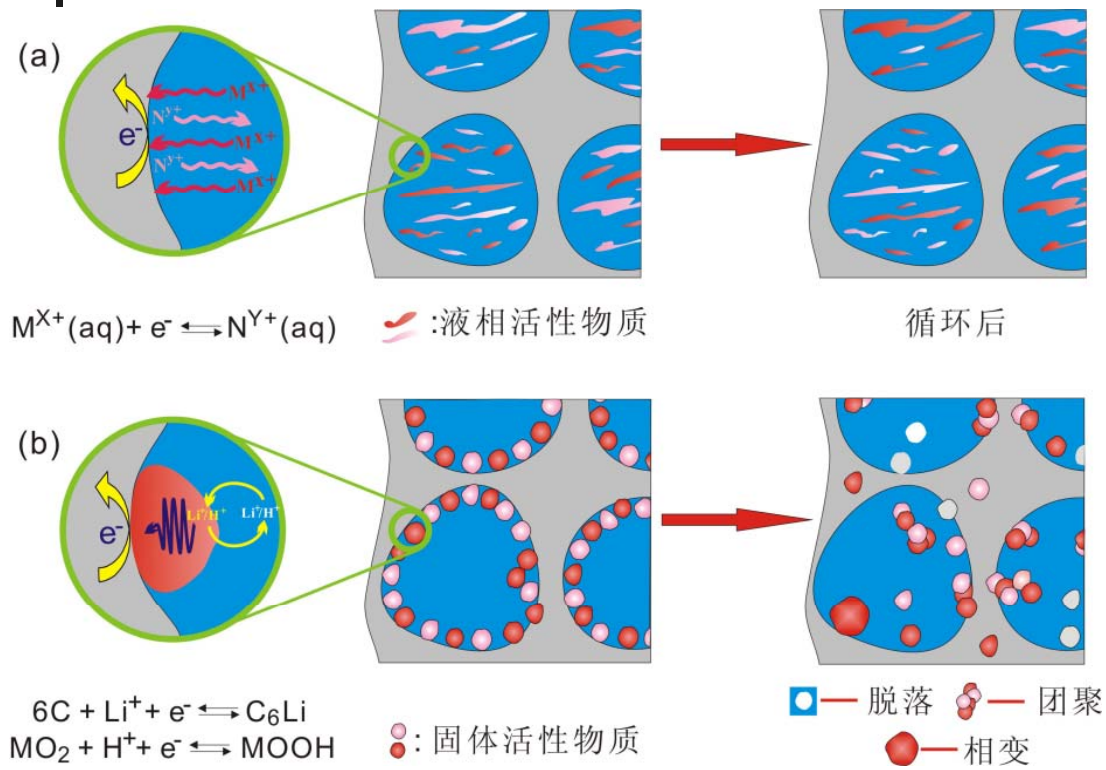
DOI:adma.201001578

High power EC energy systems

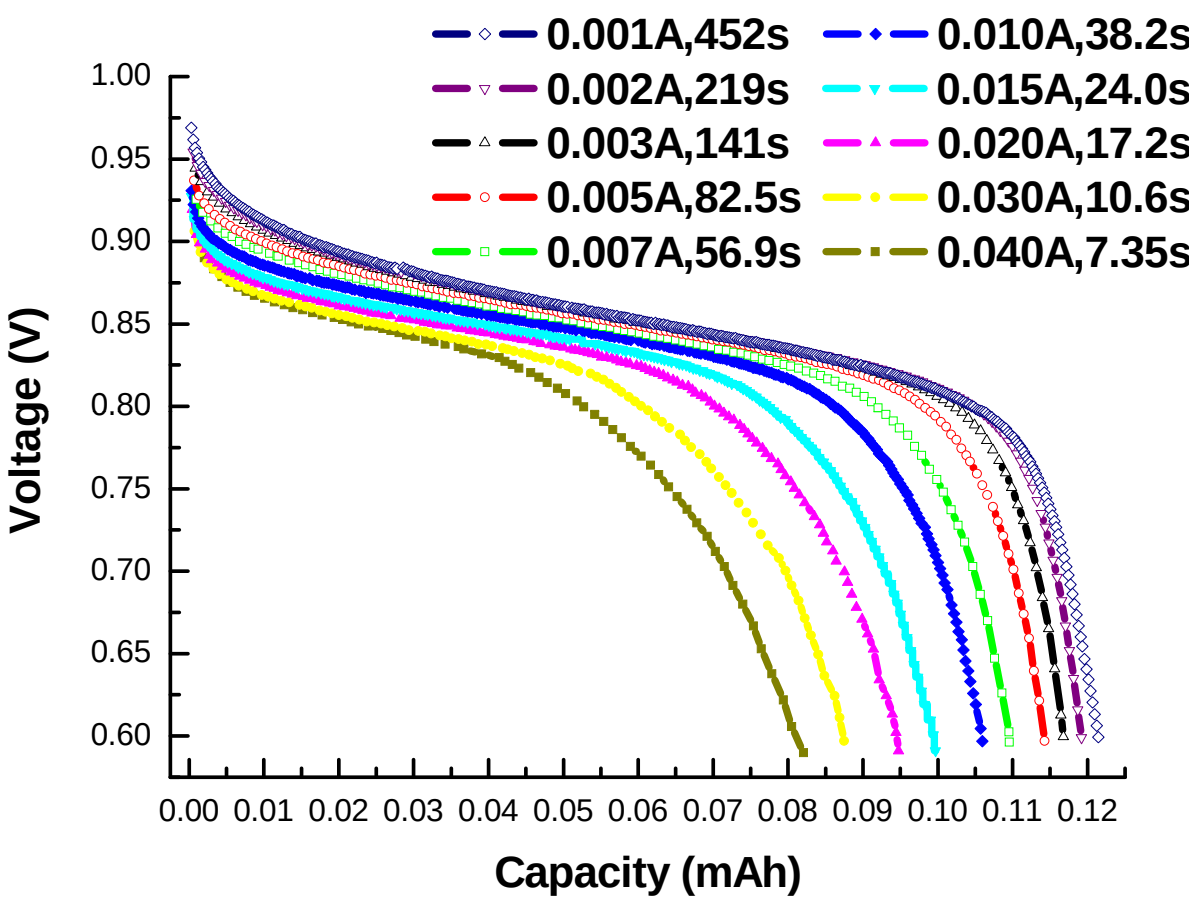


Liquid phase system

Solid phase system

国家发明专利授权（ZL200610087625.1),
美国专利（申请号：PTO 12/303,193）和欧洲专利（申请号：EPO 07720728.0）

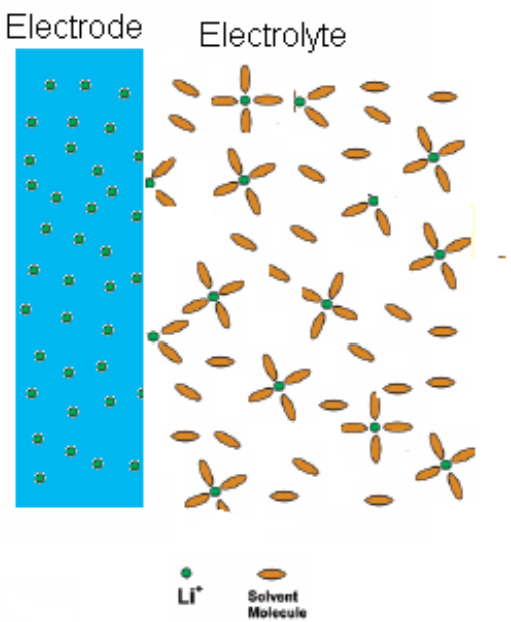
The performances



The discharge rate is increasing from 8C to 490C , the retention is 67% ,

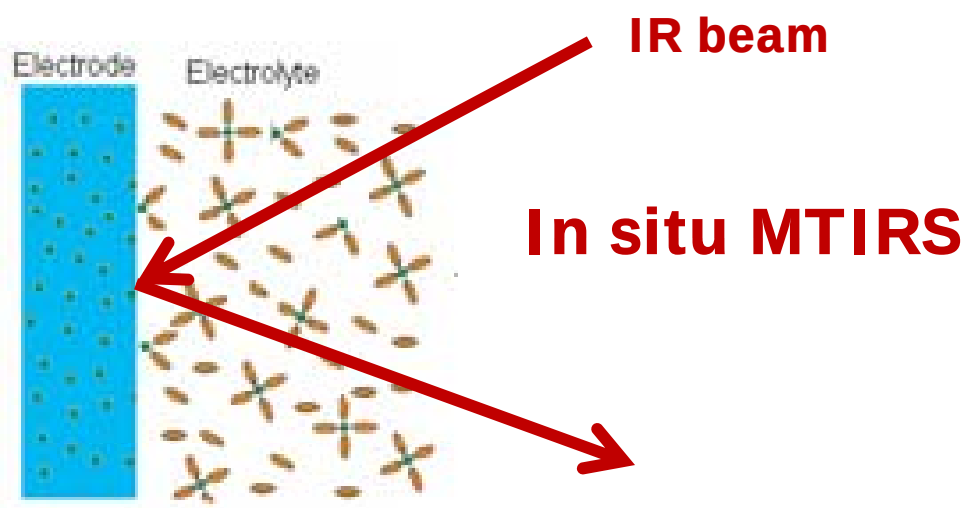
The importance of interfaces in LIBs

1. **Interfacial properties are related with reactions occurring both inside and on surface of electrode**, including Li ion intercalation/de-intercalation, decomposition of electrolyte and formation of solid electrolyte interphase (SEI).
2. **Interfacial properties determine the performance of a LIB**, such as cycleability, life time, stability, and irreversible capacity, etc.
3. **A better understanding of the interfaces of LIB is prerequisite for improving existing LIB and developing advanced LIB systems.**



The significances of investigations of LIBs' interfaces

- The investigation of interfacial is complicated by the composite electrode materials, nonaquneous electrolyte and the airproof work conditions.
- As electrons and ions are exchange at the interface of LIBs, it is important to investigate at molecular level and atomic scale.
- Study of interfaces of LIBs is of also significance in revealing the structure of nonaqueous interfaces and developing relevant models and theories.



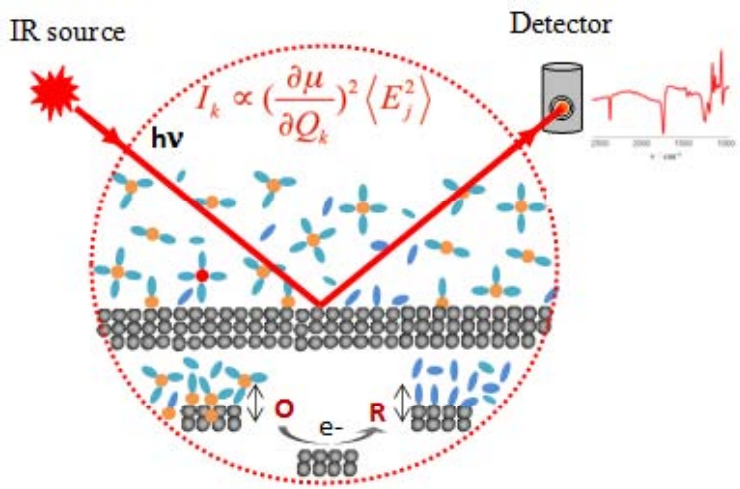
EQCM: $\Delta m = -sA\Delta f$

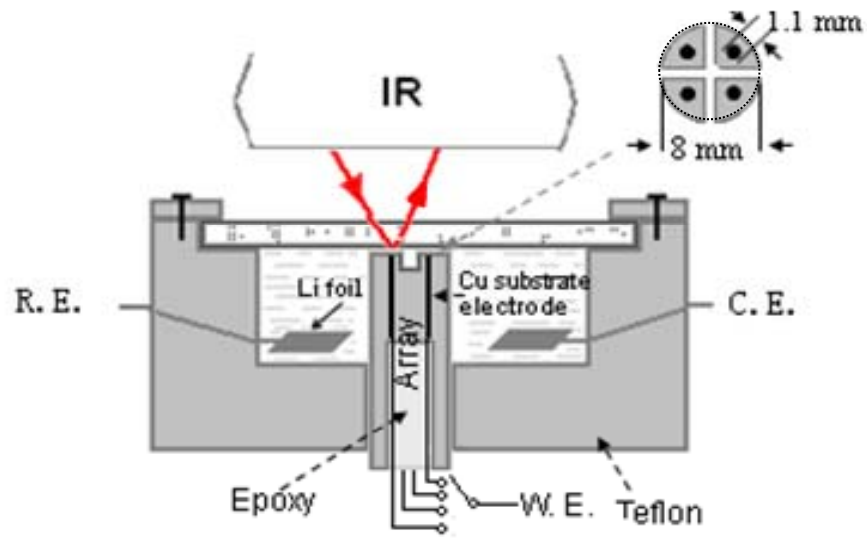
Investigation of interfaces of LIB by in situ MFTIRS and EQCM

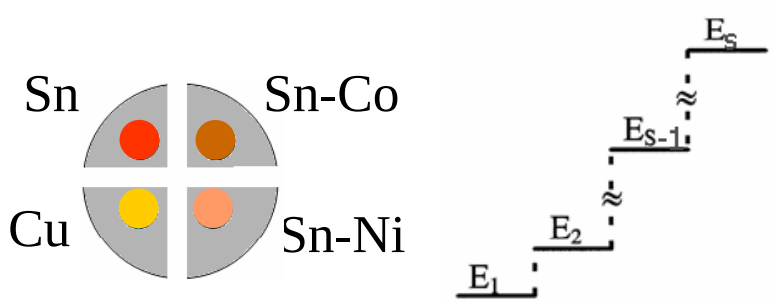
FTIRS can provide information about interfacial processes involved in electrochemical reactions at molecule level, including the chemical compositions of the SEI film.

EQCM can determine surface mass change of electrode at a nanogram range, which is applied to monitor the formation of SEI and to probe the Li ion intercalation / de-intercalation.

In situ MFTIRS and Array electrode technology







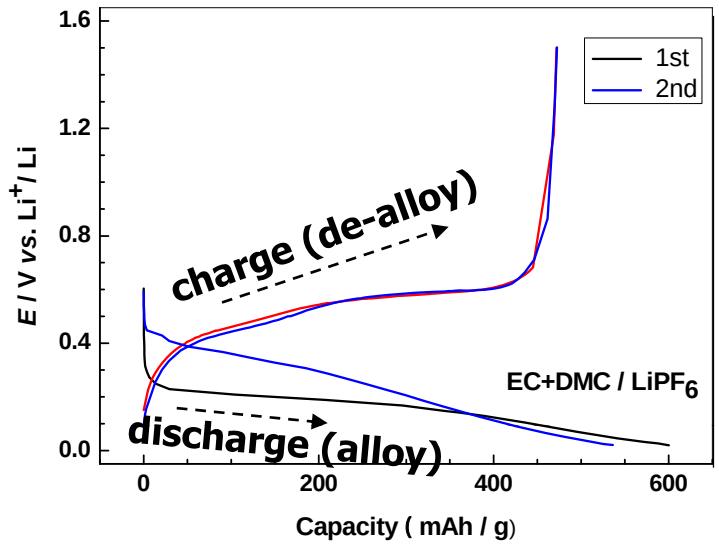
$$\frac{\Delta R}{R}(E_S) = \frac{R(E_S) - R(E_R)}{R(E_R)}$$

Electrode array: Different composition of metal (alloy) films were deposited electrochemically on the array of Cu substrate microelectrode.

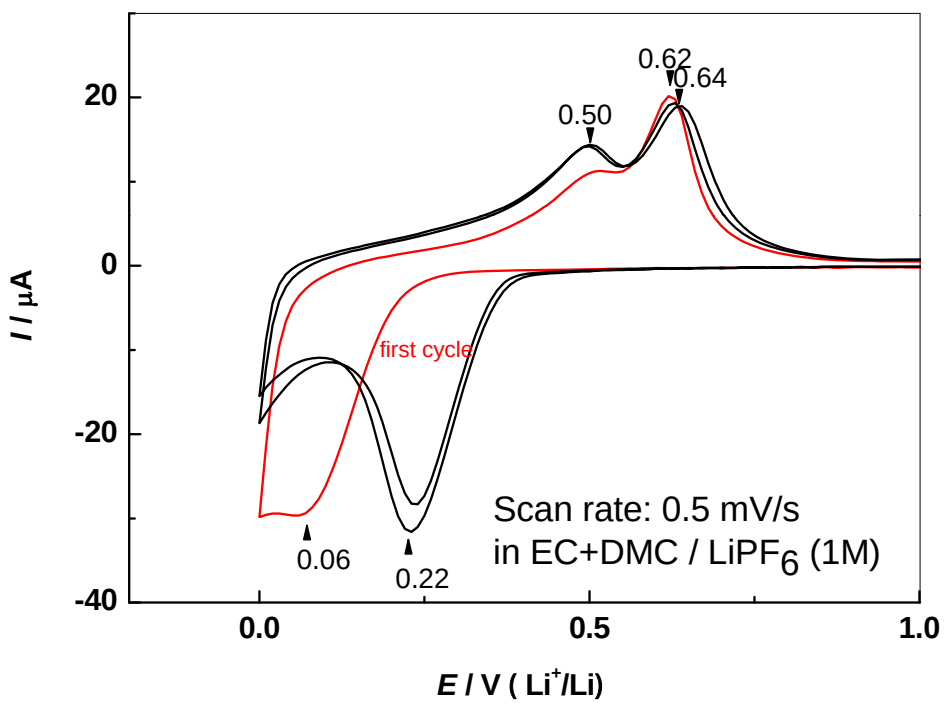
In-situ MFTIRS cell: airproof, Li foil counter and reference electrodes.

Electrochemical properties Sn-Co alloy electrode

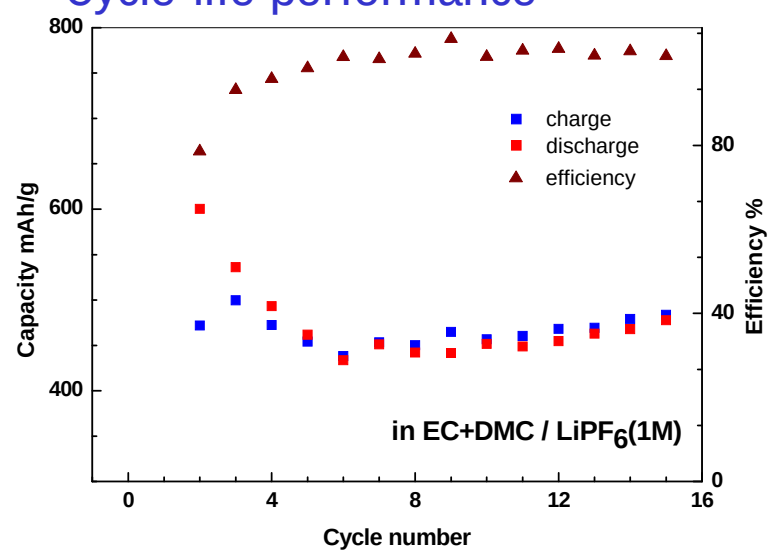
Charge–discharge curve of first 2 cycle



CV curve of Sn-Co electrode

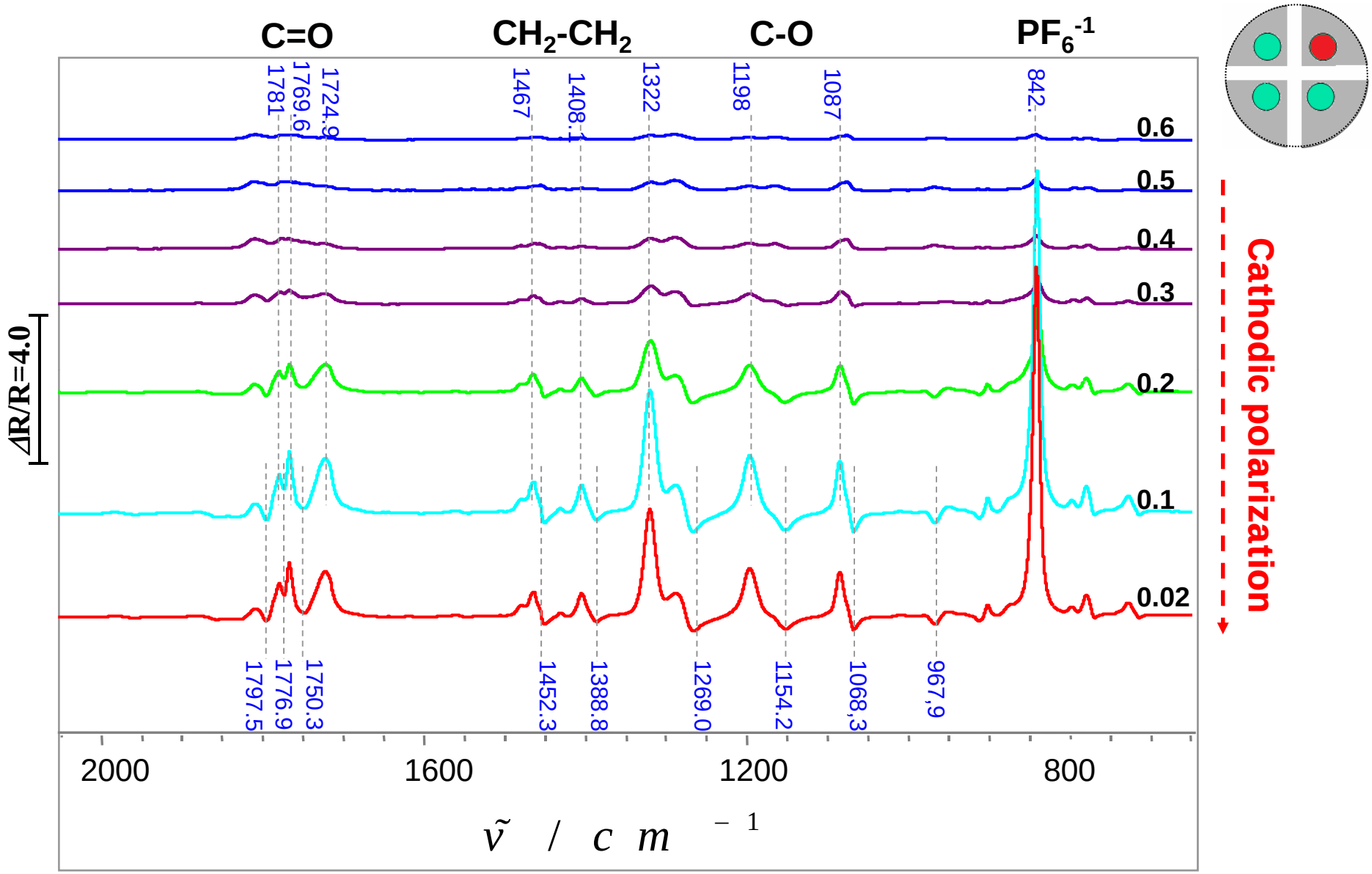


Cycle-life performance



$$CoSn_2 + 2xLi(sol)_n^+ + 2xe^- \underset{\text{de-alloy}}{\overset{\text{alloy}}{\rightleftharpoons}} 2Li_xSn + 2Co + 2nx\ sol\ (x = 0 \sim 4.4)$$

In situ MFTIRS of Sn-Co alloy electrode during Li alloying process



$$\frac{\Delta R}{R}(E_S) = \frac{R(E_S) - R(E_R)}{R(E_R)}$$

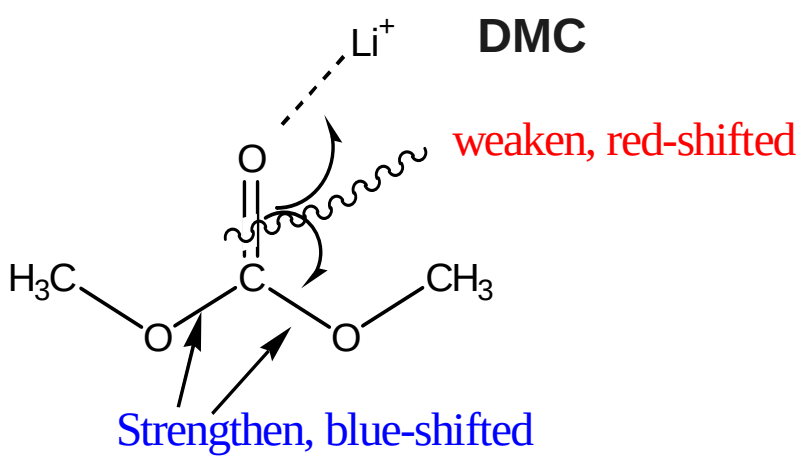
J. Electroanalytical Chem. 2010 , In press.

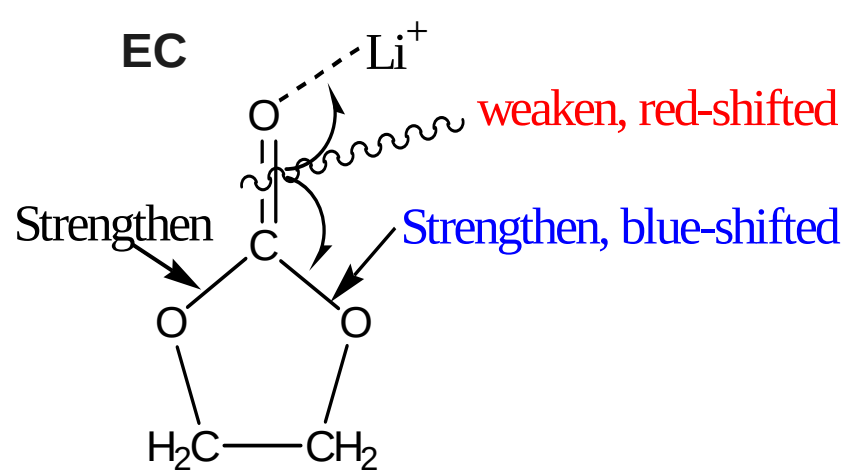
$$CoSn_2 + 2xLi(sol)^+ + 2xe^- \xrightarrow[\text{Cathodic polarization}]{\text{de-alloy}} 2Li_xSn + 2Co + sol \ (x = 0 \sim 4.4)$$

In the charge process (cathodic polarization)

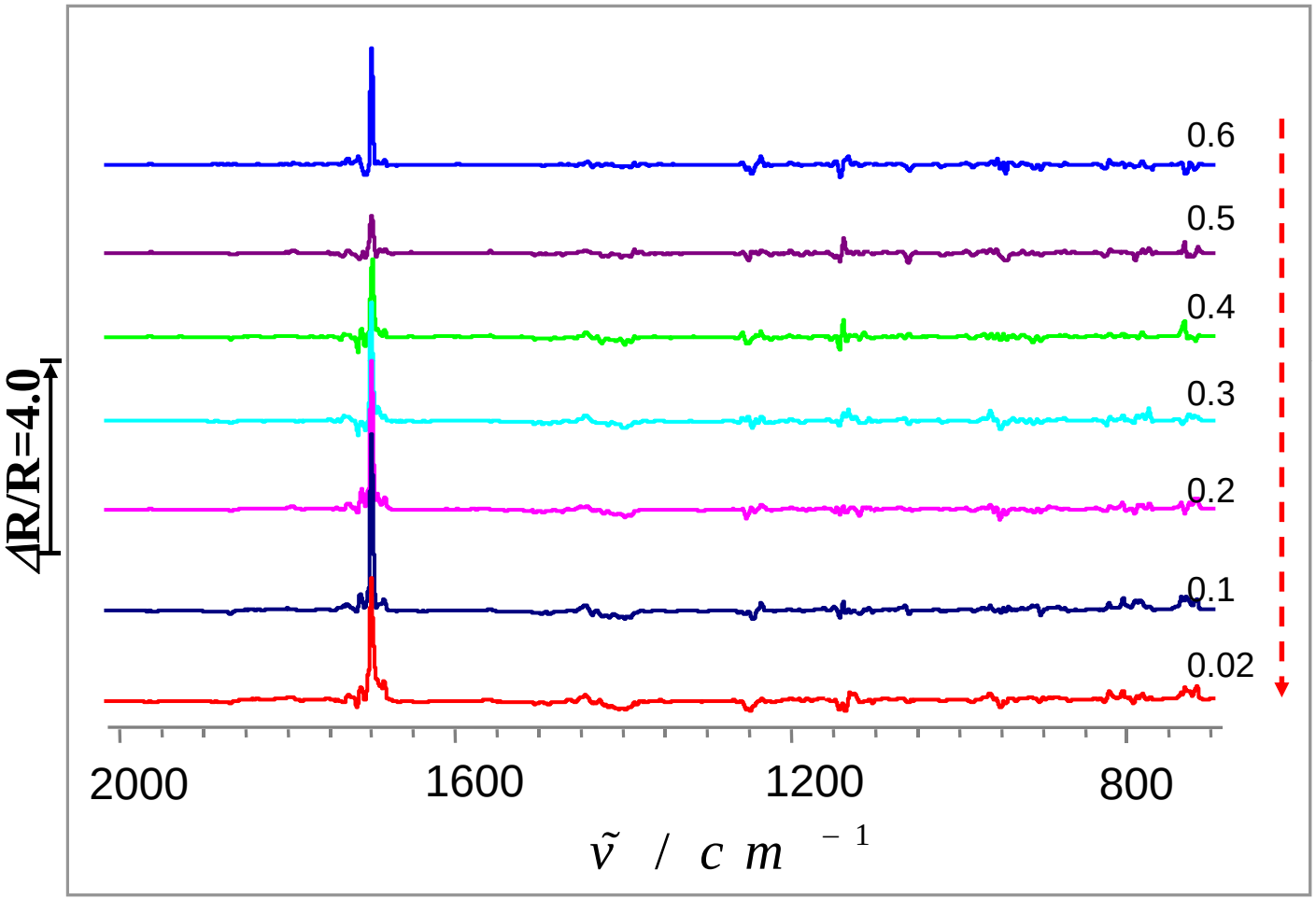
1. Li ion de-solvation from $Li(sol)_n^+$ to alloy with Sn-Co.
2. The concentration of un-solvated solvents increase, while $Li(sol)_n^+$ decrease in the thin layer.
3. The concentration of PF_6^{-1} decrease to keep the electric balance of thin layer.
4. Shift of IR bands (C=O,C-O,C-H…)

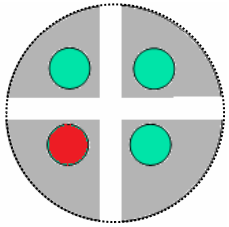
The shift of IR bands occurs between solvated and un-solvated solvents





In situ MFTIRS of Cu electrode on the array in the same experimental conditions



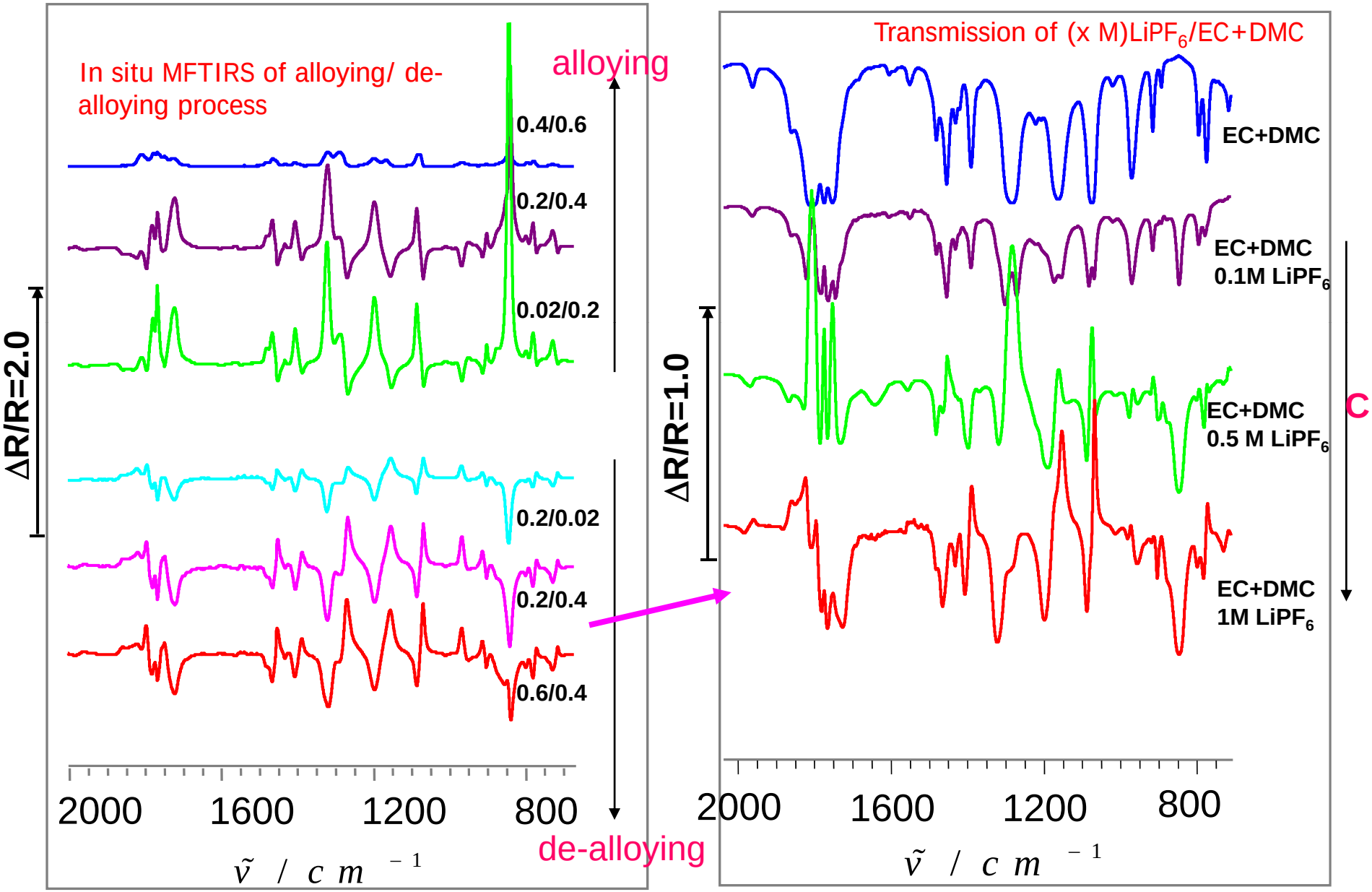


The Cu electrode on the array. Under the same experiment conditions, we do not see significant IR bands change, because Li ion can not alloy and de-alloy with Cu electrode

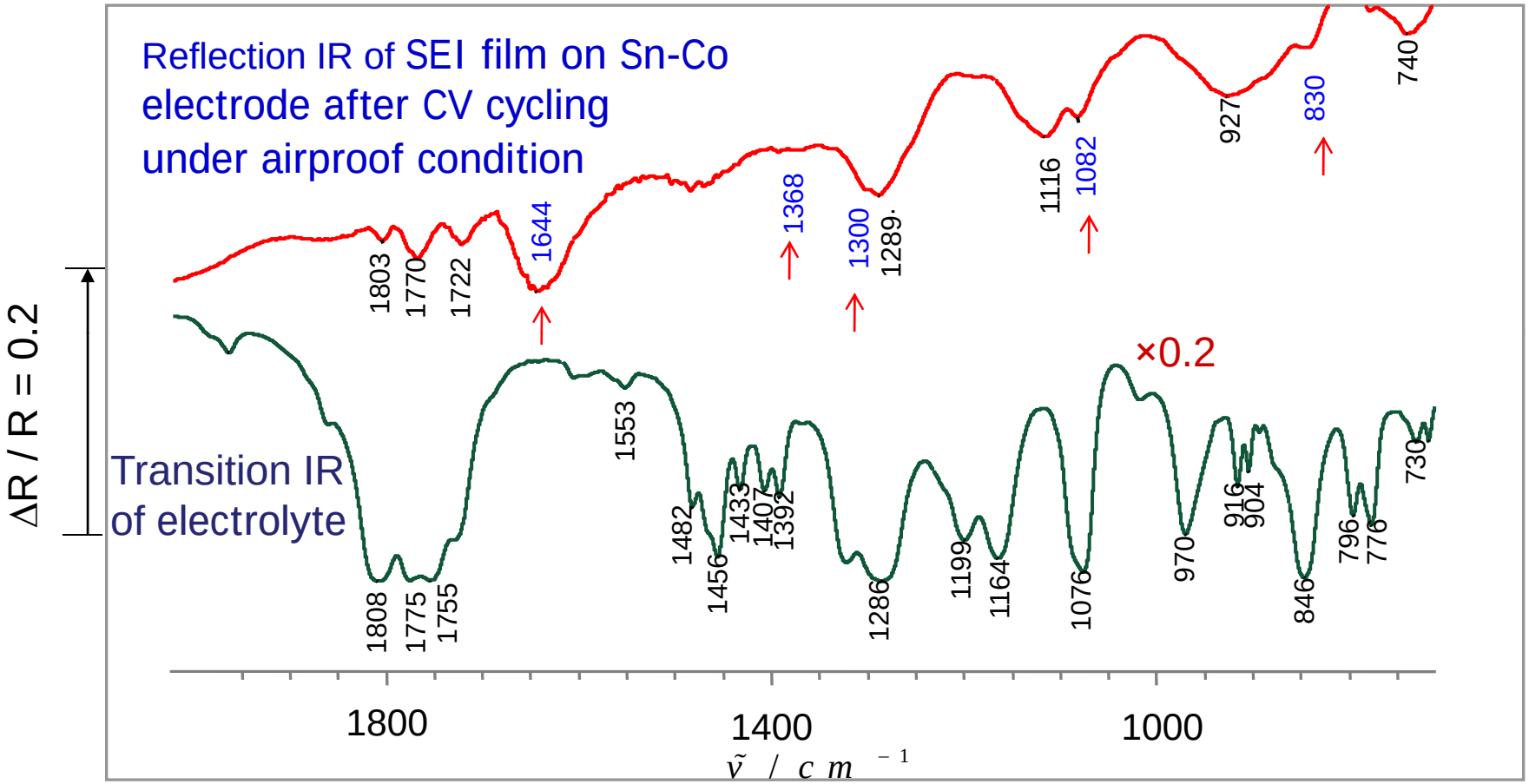
$$\frac{\Delta R}{R}(E_S) = \frac{R(E_S) - R(E_R)}{R(E_R)}$$

E_R=0.7 V *vs*. Li^+/Li , in EC+DMC/$LiPF_6$ (1M)

In situ MFTIRS of alloying and de-alloying process and Transmission FTIRS of EC+DMC/ $LiPF_6$ (x M)



Ex-situ MFTIRS of chemical composition on Sn-Co alloy electrode after CV cycling



The main composition of SEI on Sn-Co alloy thin film after cycling in 1 M $LiPF_6$ / EC+DMC (1:1) is $(CH_2OCOOLi)_2$ (reductive products of EC) that yields IR bands at 1644,1368,1300,1082,830 cm^{-1}

Studies of in situ Microscope FTIRS

- Interface properties between Sn-Co electrode and electrolyte

  (A) Interface properties during Li ion alloying / de-alloying process.

  (B) Chemical composition of SEI.

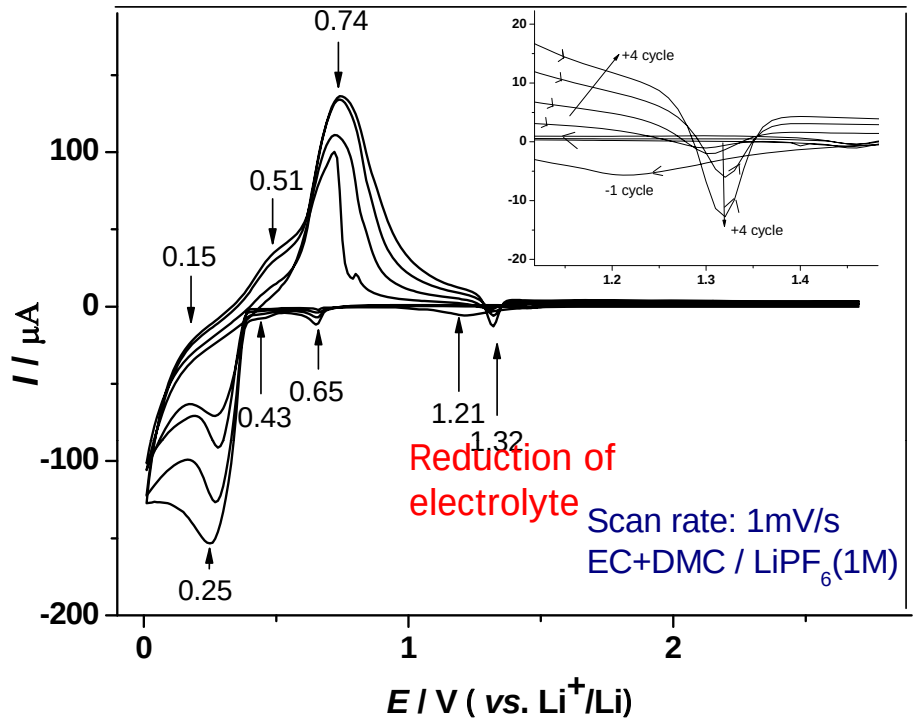
- Interface properties between Sn electrode and electrolyte

  (A) Interface properties during Li ion alloying / de-alloying process.

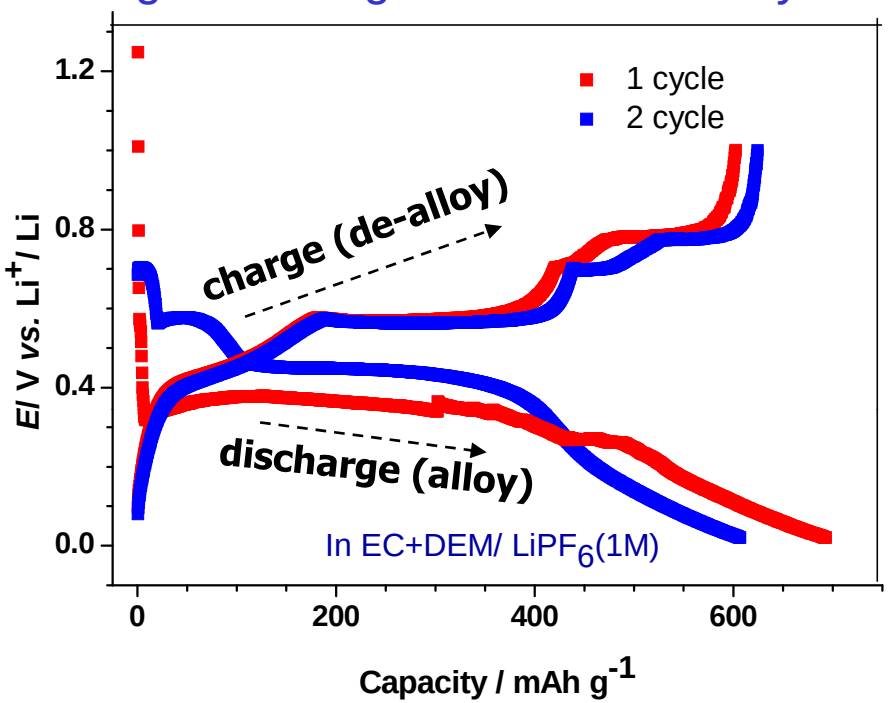
  (B) Interface properties during the decomposition of electrolyte.

Electrochemical properties of Sn electrode

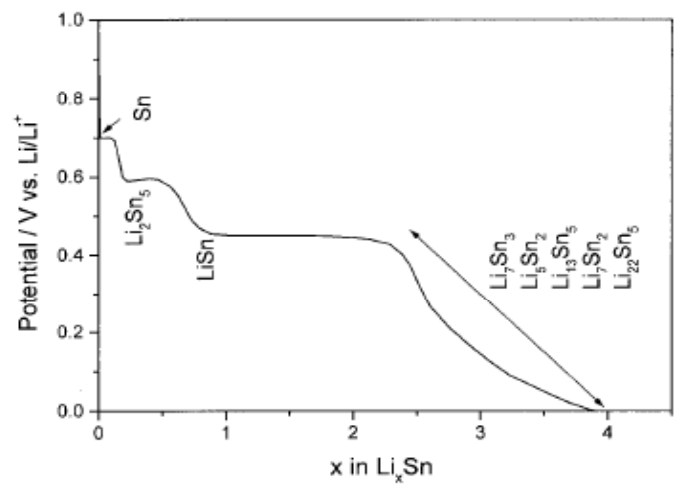
CV curve of Sn electrode



Charge–discharge curve of first 2 cycle

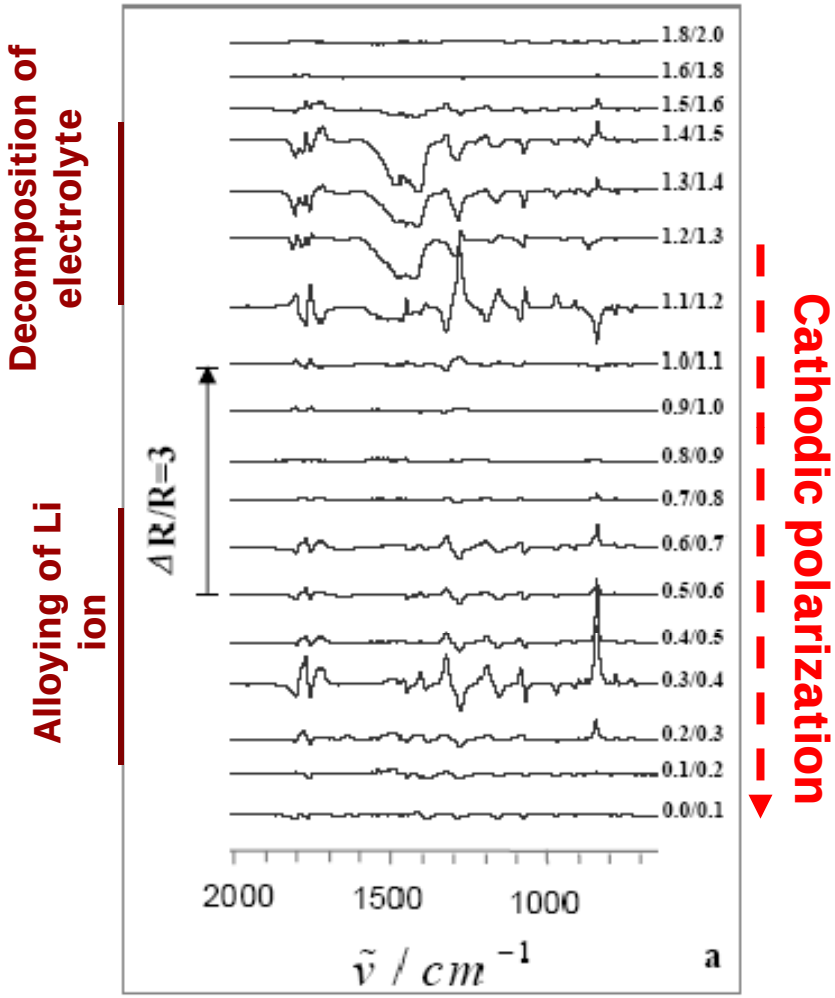


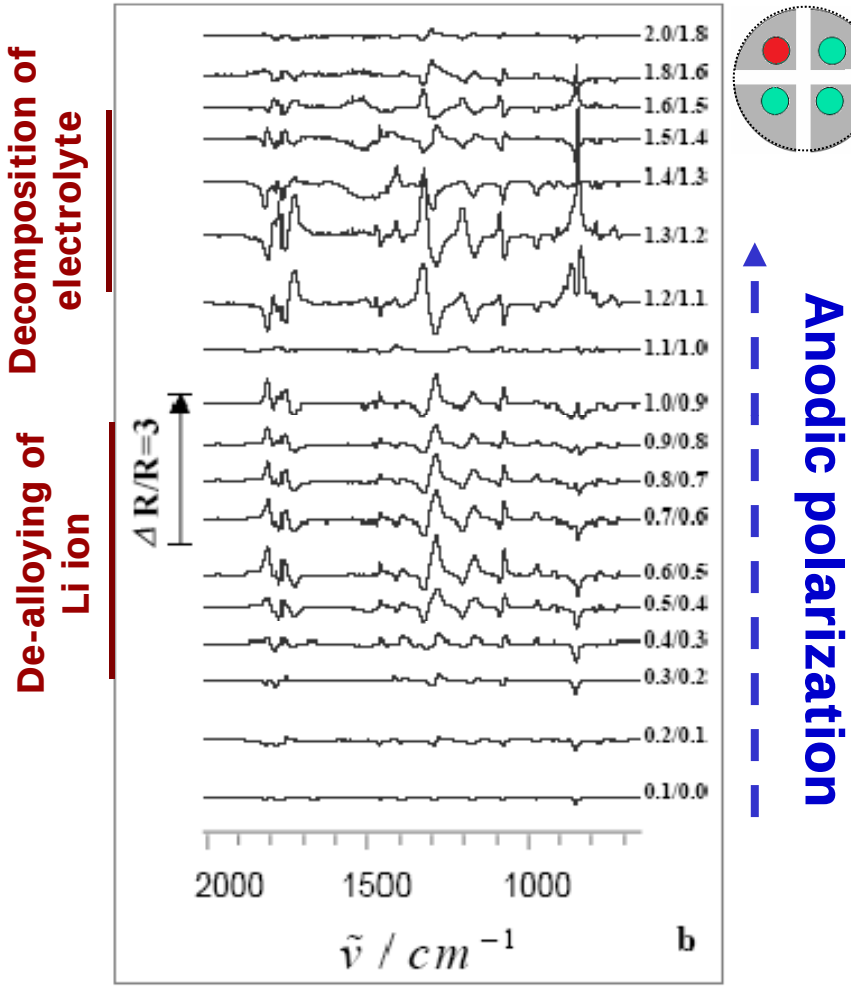
$$Sn + Li(sol)_n^+ + xe^- \underset{\text{de-alloy}}{\overset{\text{alloy}}{\rightleftharpoons}} Li_xSn + x\ sol\ (x=0\sim4.4)$$



Langmuir, 2007, 23, 13174.

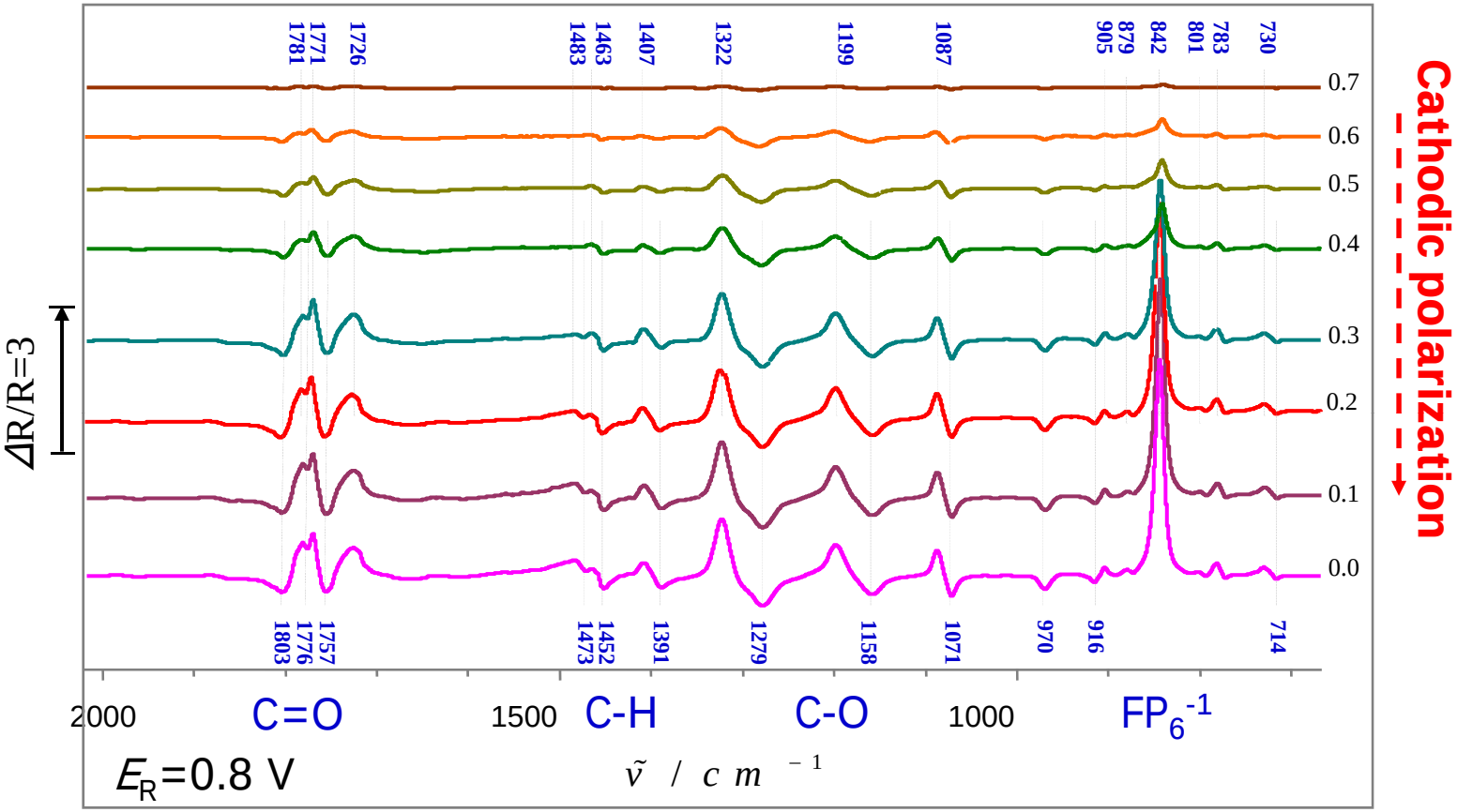
Comprehensive sets of in situ MFTIR spectra of Sn film electrode





Each spectrum is calculated by taking the single-beam spectrum collected at previous potential as the reference. In 1M $LiPF_6$ / EC+DMC(1:1)

Alloying process of Li ion (cathodic polarization)

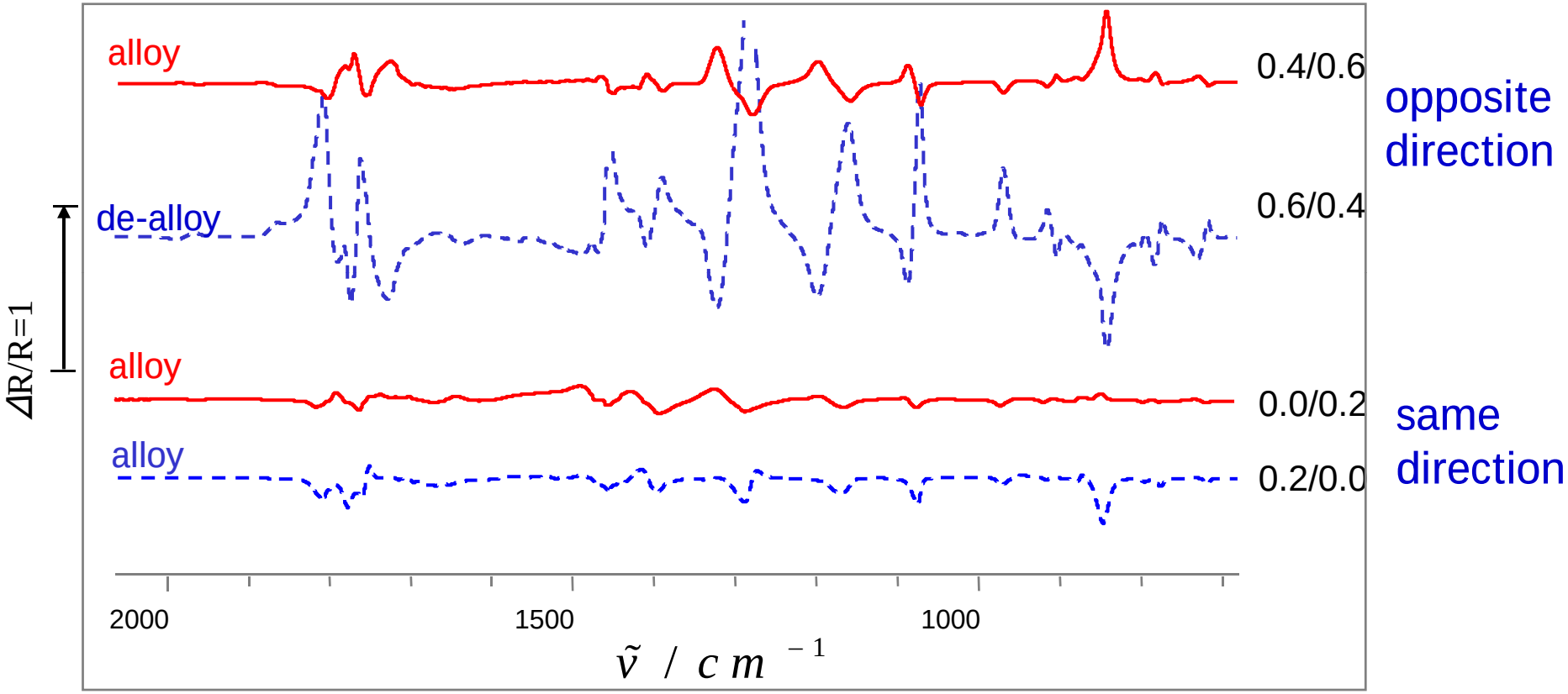


◆**Concentration change:** **Li(sol)$_n^+$,EC, DMC, LiPF$_6$**

◆**Bands shift of C=O,C-O and C-H.**

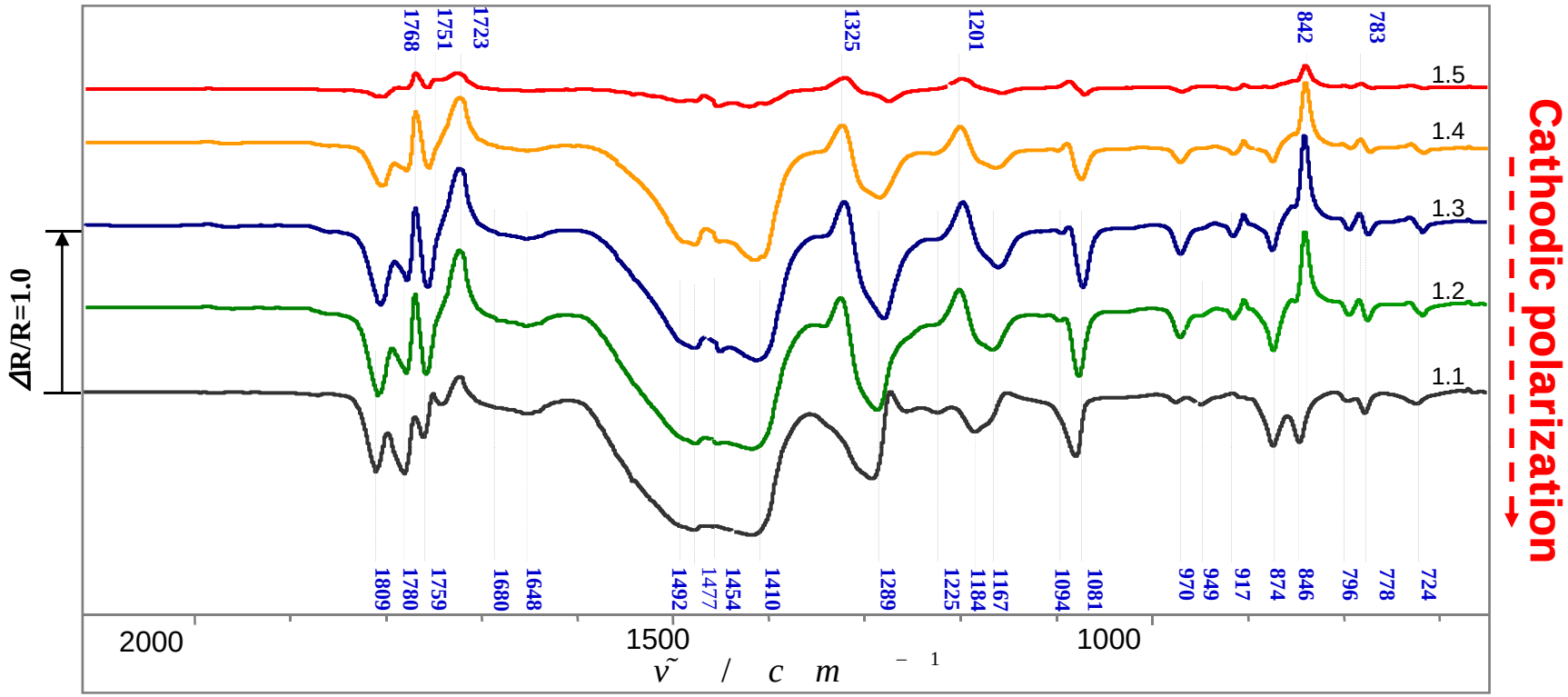
◆**Upward bands are stronger than the downward bands:** **Most of solvent is un-solvated, only part of solvent exists in Li(sol)$_n^+$ form.**

Comparison of alloying and de-alloying processes



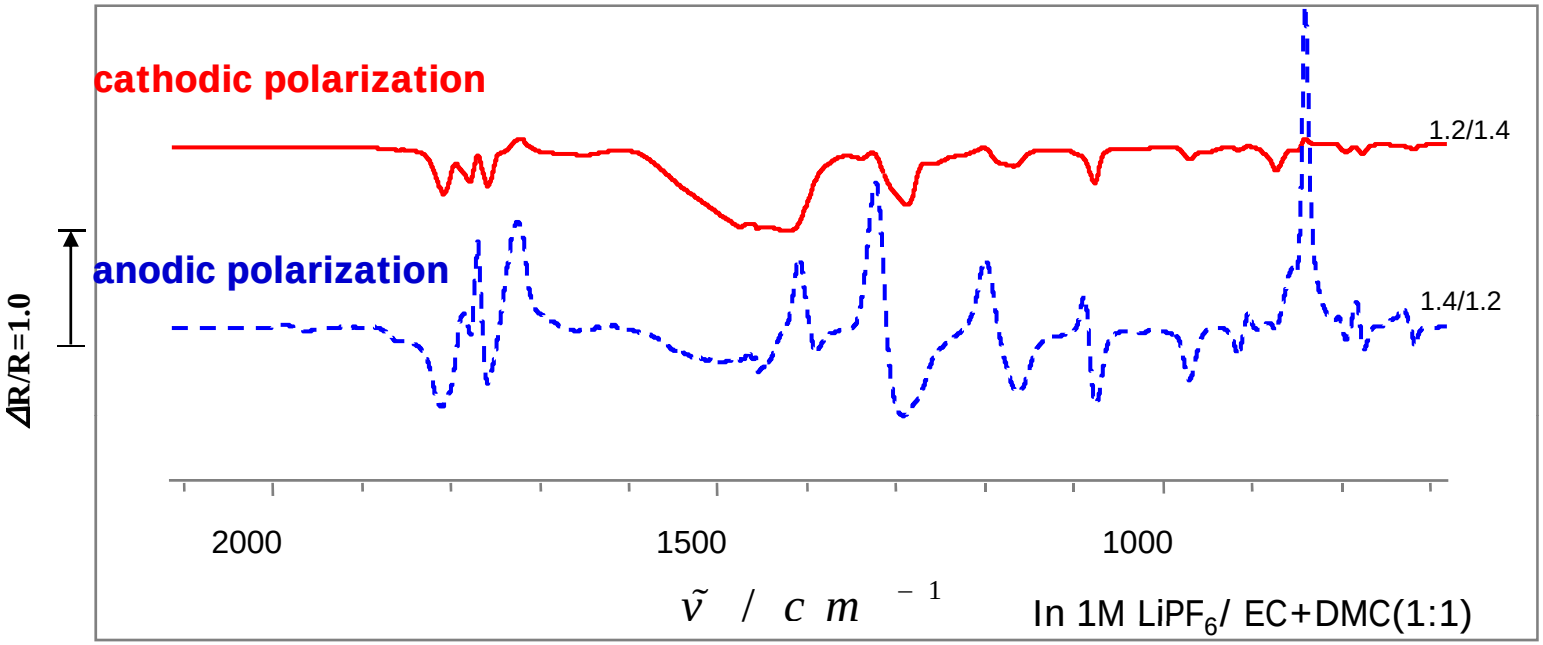
$$Sn + Li(sol)_n^+ + xe^- \underset{\text{de-alloy}}{\overset{\text{alloy}}{\rightleftharpoons}} Li_xSn + x\ sol\ (x = 0 \sim 4.4)$$

Reductive decomposition of electrolyte (cathodic polarization)



- New downward bands at 1680, 1648, 1225, 1184, 1094, 949, 846 cm^{-1} are assigned to the reduction product of the ROCOOLi.
- The upward bands in the spectra are assigned to the consumption of $Li(sol)_n^+$, So it is $Li(sol)_n^+$ rather than un-solvated molecules to reduce on the electrode.
- Different from alloying / de-alloying process, most bands in the spectra are downwards. Because when $Li(sol)_n^+$ reduce to solid products, solvent (EC and DMC) diffuse from bulk into the thin layer, leading the increase of both solvent and reductive products.

Comparison of cathodic / anodic polarization during electrolyte reduction



$$Li(sol)_n^+ + xe^- \xrightarrow{\text{reduction}} ROCOOLi$$

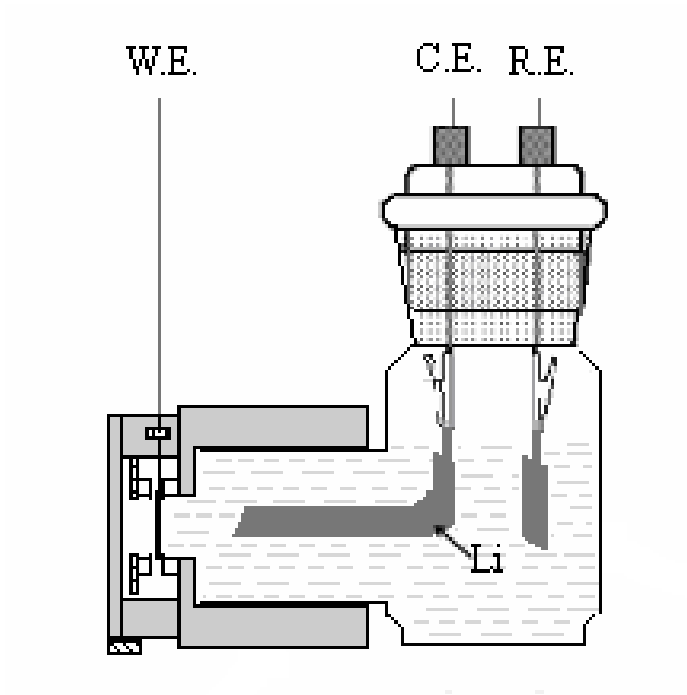
IR bands in the two spectra appearing at the same wavenumber and in the same direction, implying that the same interfacial reaction (reduction of electrolyte) was taken place no matter the electrode potential is cathodic or anodically polarized.

Summery of in situ MFTIRS results

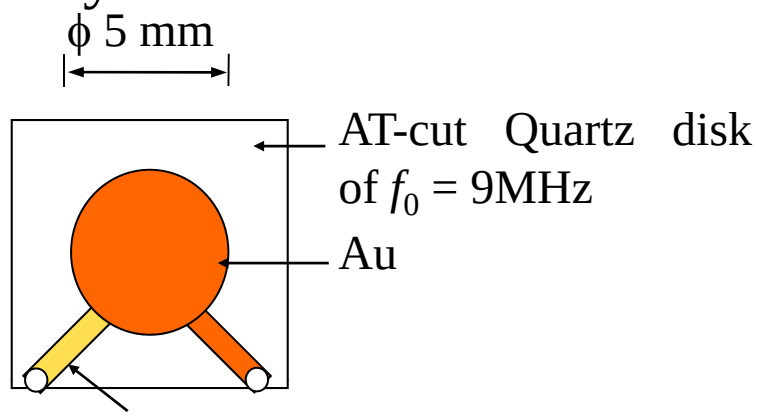
- Interfacial reactions in LIB during the cathodic/anodic polarization were clearly characterized;
- In-situ MFTIRS is a powerful new approach for LIB investigation, consisting in the phase transition process and the solvation / de-solvation of Li ion with solvent;
- The results about chemical composition of the SEI as well as the decomposition of electrolyte are helpful for analyzing the mechanism of SEI formation on Sn (alloy) electrode.

Nonaqueous interface of LIB investigated by EQCM

Basing on the piezoelectric effect of a quartz crystal



EQCM cell



EQCM electrode.

Sn electrode used in EQCM was electrodeposited on Au substrate electrode. About 30 mg·cm^{-2} of Sn has been deposited assuming that the coulomb efficiency is 100%.

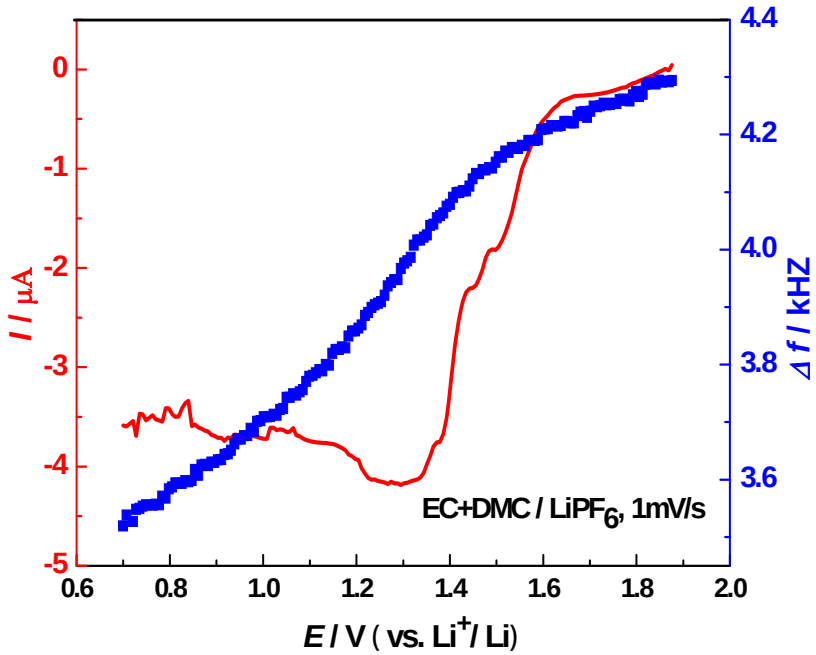
$$dm = -sAdf$$

$$mpe = -sFA\frac{df}{dQ} = -sFAk \ (\mathrm{g \cdot mol^{-1}})$$

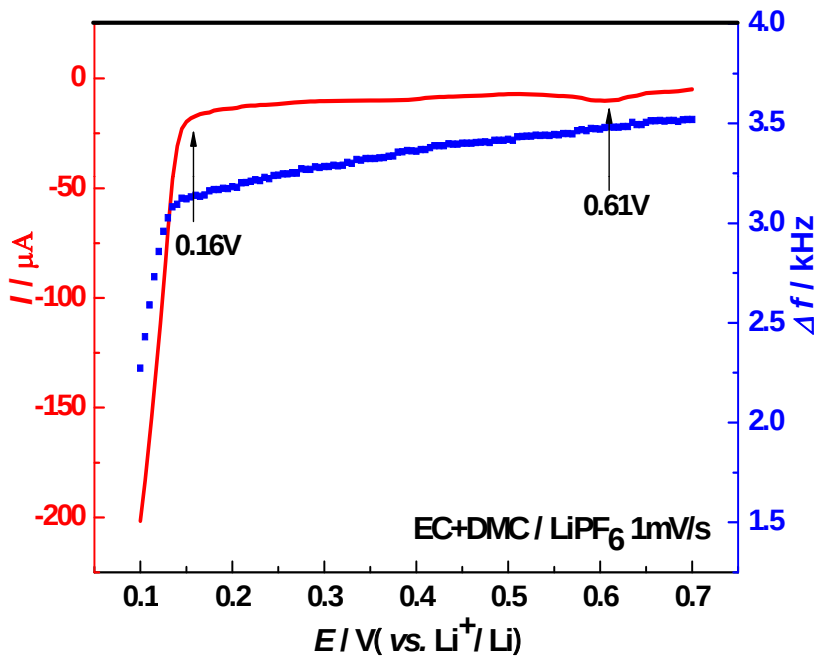
mpe: mass accumulated on electrode per mole of electrons

EQCM study of Sn thin film electrode supported on quartz during the first negative scanning

In the region of electrolyte reductive decomposition



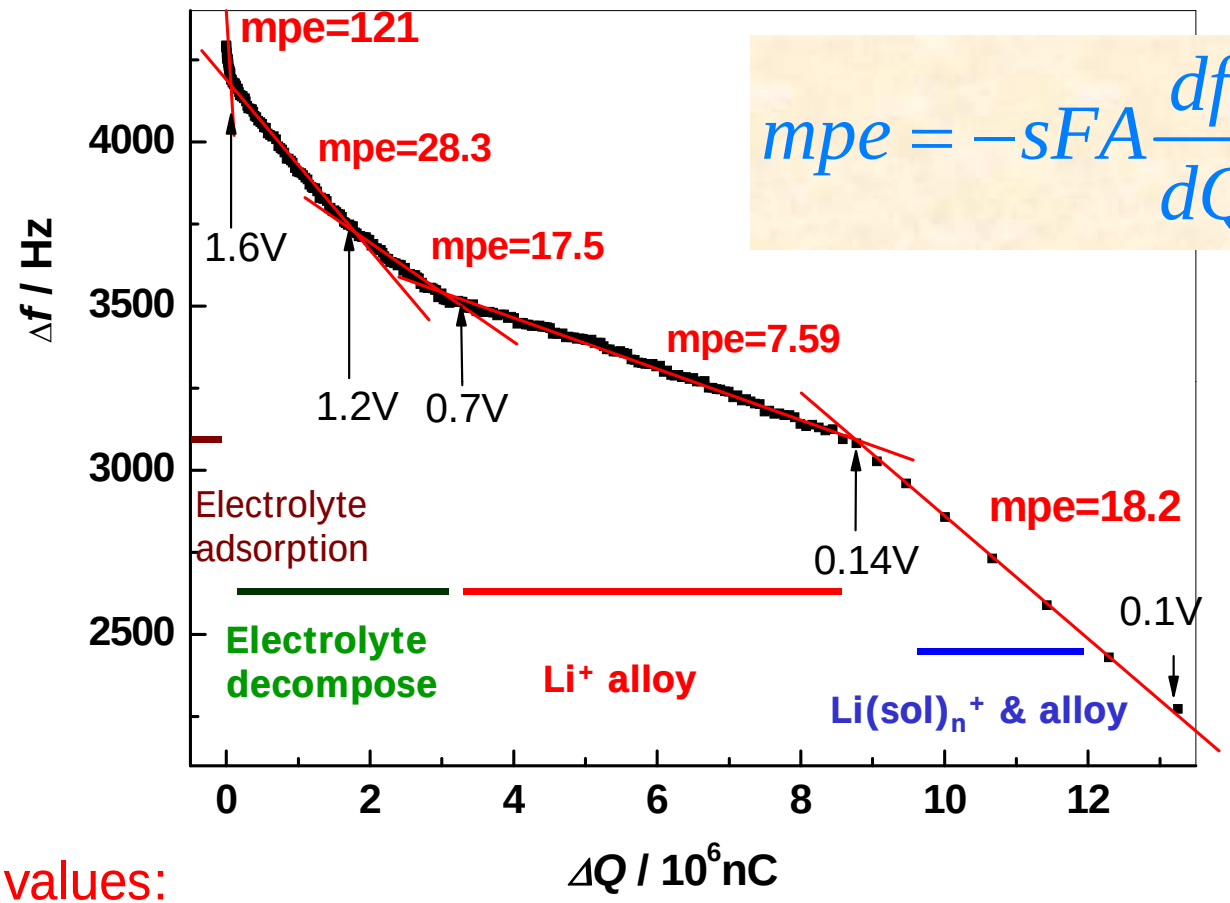
In the region of alloying of Li ion with Sn



The increase in mass on electrode corresponds to a decrease in resonant frequency

Langmuir, 2007, 23, 13174.

Plot of Δf versus ΔQ and measured mpe



$$mpe = -sFA\frac{df}{dQ} = -sFAk$$

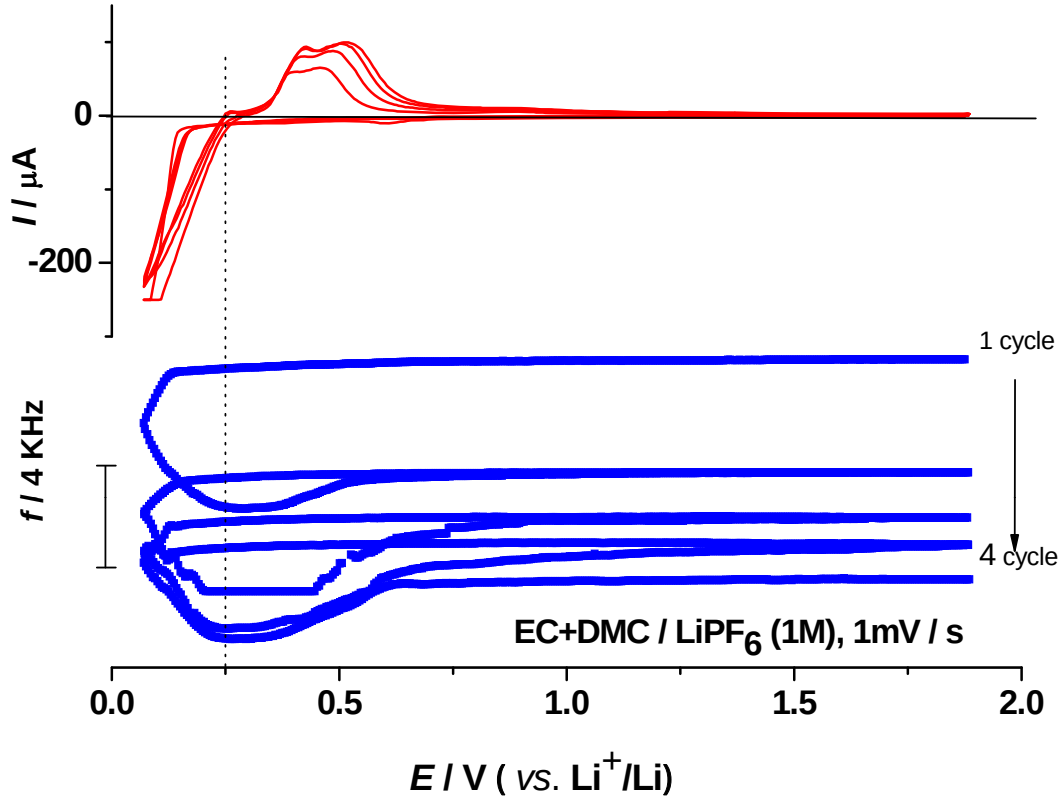
Theoretical values:

(De)-alloying of Lithium: *mpe* (Li^+)= 6.9 g·mol^{-1}

EC reductive producsts: $(CH_2OCO_2Li)_2$(*mpe*:81); Li_2CO_3(*mpe*:37)

DMC reductive products: CH_3OLi (*mpe*: 38); CH_3OCO_2Li (*mpe*: 82)

EQCM study of Sn thin film electrode supported on quartz



Cycle number	*mpe* (g/mol) in different Potential region (V)				Unbalanced Mass / μg
	0.7-0.14	0.14-0.07	0.07-0.25	0.3-1.0	
1	7.5	18.2	10.0	-10.8	4.59
2	7.0	10.2	13.4	-22.5	1.83
3	8.5	10.8	16.1	-7.9, -15.3	1.26
4	8.3	8.3	15.1	-9.1, -12.8	1.26

Summery of EQCM results

- The values of *mpe* were varied in the charge/discharge process, which illustrated different electrochemical processes.
- When electrolyte is reduced, the measured *mpe* is smaller than the theoretical value, due to that part of decomposed products is dissolved into solution and some solvent molecules were adsorbed on electrode before the reduction.
- In the alloying / de-alloying process, the measured *mpe* is larger than the theoretical value, indicating that solvated Li ion ($Li(sol)_n^+$) may co-alloy and de-alloy with Sn electrode.

Conclusions

- The interfacial properties of LIB in the charge/discharge process were successfully studied by developing in situ MFTIRS and EQCM at molecular level and with determination of surface mass change;
- The (de)intercalation of Li ion, the formation and the chemical composition of SEI film, the decomposition of electrolyte, and (de)solvation of Li ion with solvent were clearly characterized;
- The results have gained an insight into understanding the mechanism of SEI film formation and lithium (de)intercalation process, and are of significance in developing relevant fundamental aspects of the LIB;
- The study is of also importance in exploitation of new materials and in development of green rechargeable batteries with high-specific energy density.

Acknowledgements

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国家自然科学
基金委员会
National Natural Science
Foundation of China

Thank you for your attention !