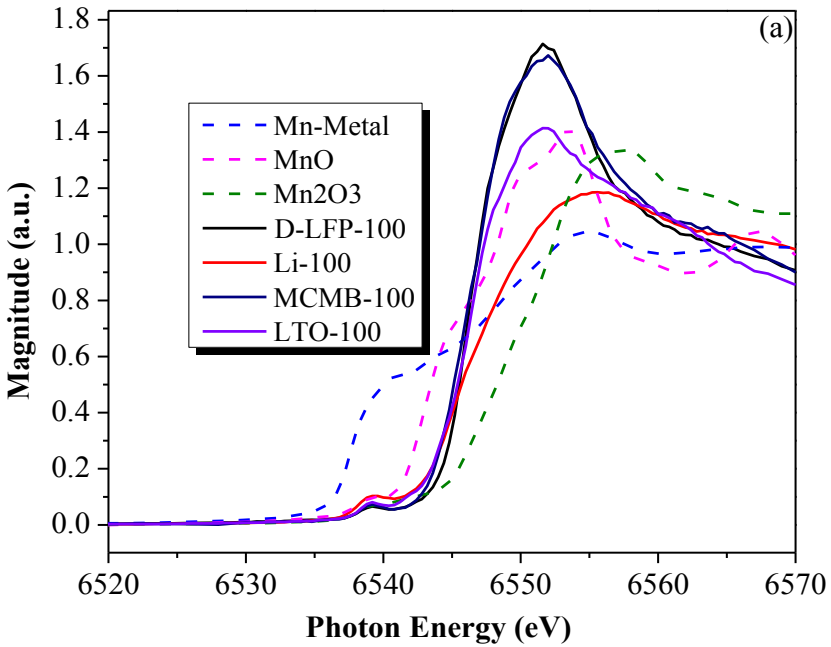
X-ray Absorption Spectrum (XAS) on Anodes (XANES)



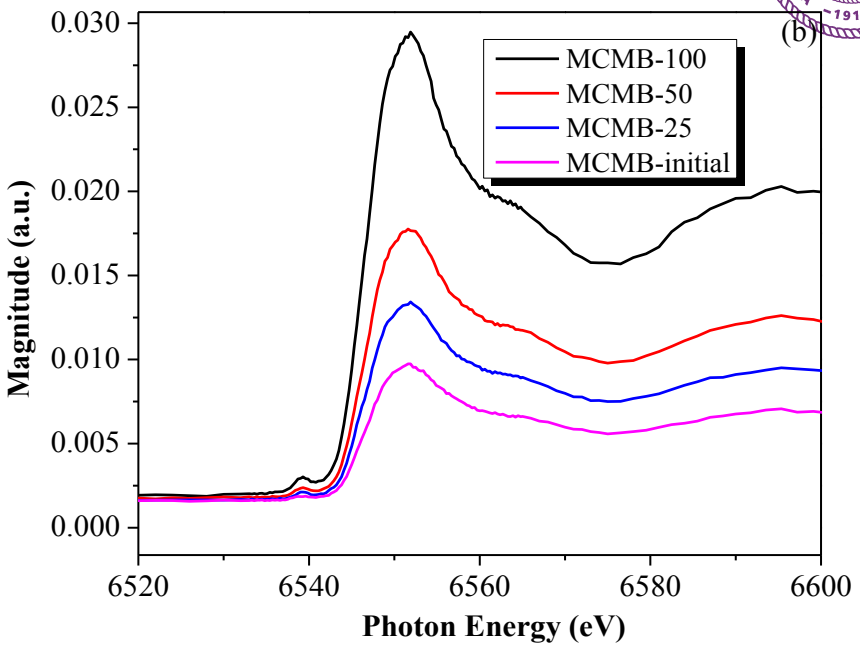


Fig. 3 (a) Normalized X-ray absorption near edge spectra (XANES) of Mn K-edge for commercial MnO, Mn_2O_3, Mn foil, and different anode samples harvested after 100 cycles, and (b) unnormalized XANES of Mn K-edge MCMB anode samples harvested after different cycles

- Oxidation state of Mn deposited on all of the anodes is 2+!!!
- Mn oxidation state deposited on the anodes does not depend on their chemical potential and chemical activity during the discharge/charge process

X-ray Absorption Spectrum (XAS) on Anodes (EXAFS)

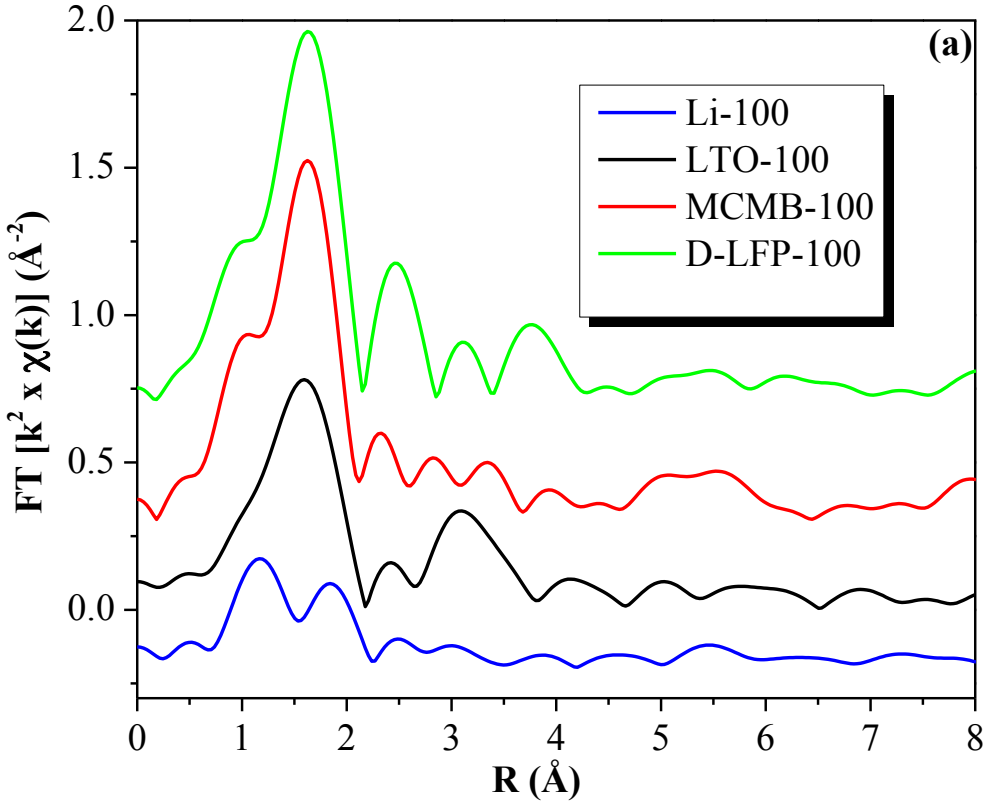
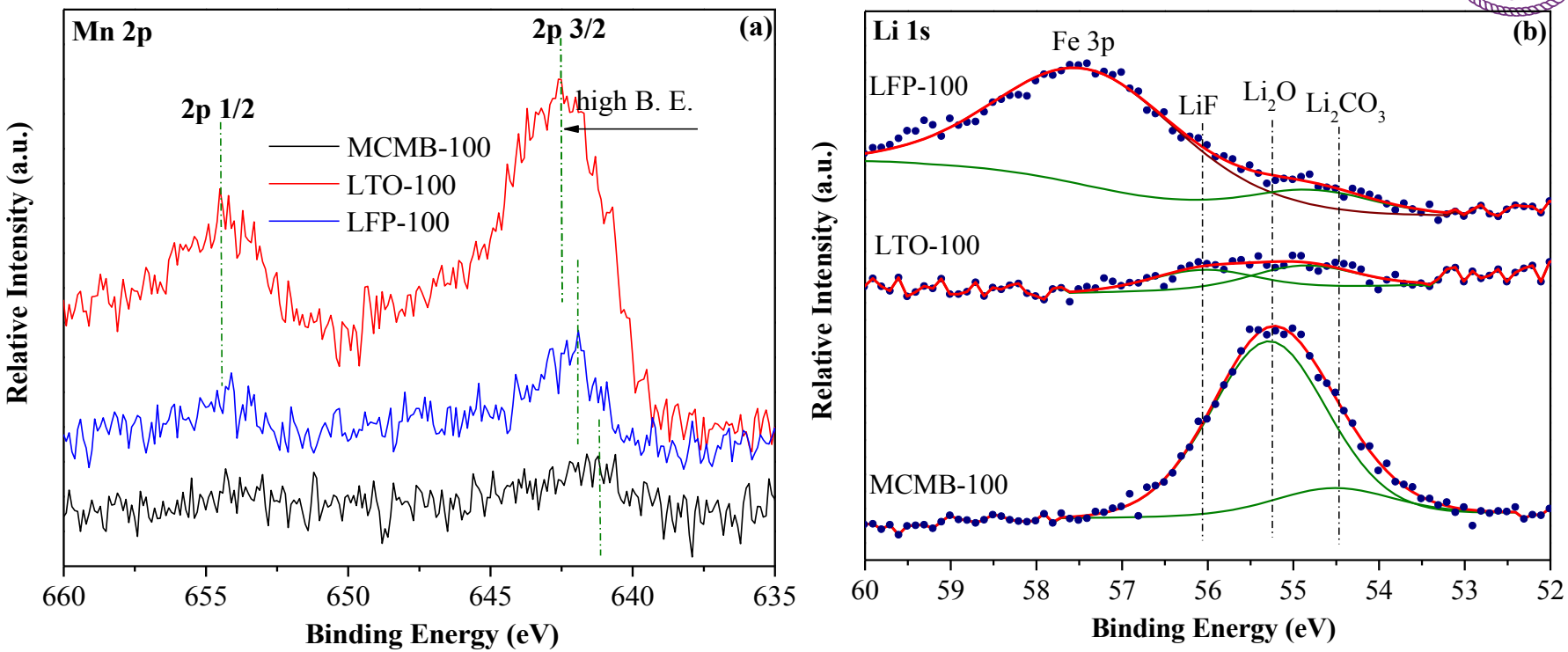


Fig. 4 Fourier transforms of the absorption spectra ($\chi(k) \times k^3$ function) for different anode samples harvested after 100 cycles

- Mn-O bond distance in LTO, MCMB, D-LFP is within 2.15±0.03 Å, but shorter than MnO (2.22 Å)
- Mn deposited on Li anode shows completely different bond length, indicating different Mn species are formed on Li anode

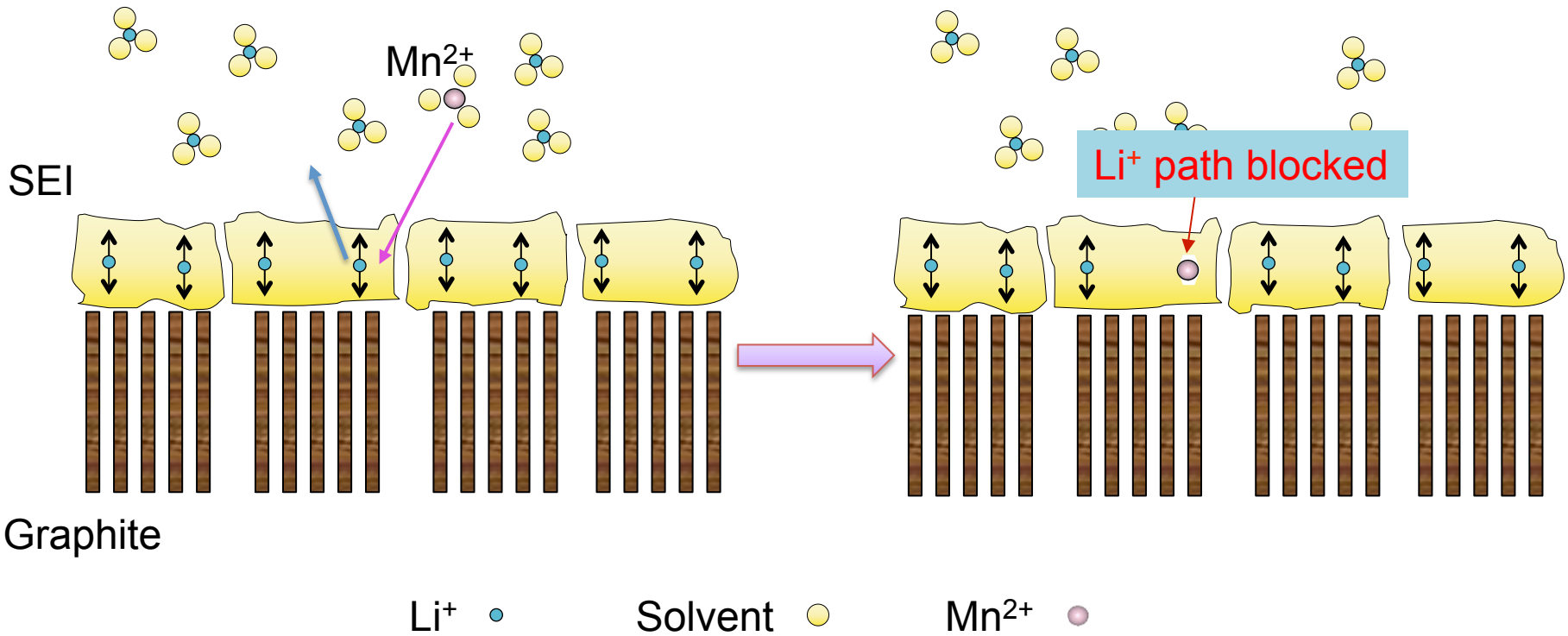
X-ray Photoelectron Spectrum on anodes (XPS)



- Mn deposited on the anodes as Mn^{2+}, consistent with the XANES results.
- MCMB anode has less Mn deposited while LTO has much more Mn deposited on the surface.
- Li amount in the SEI formed on the carbon surface after 100 cycles accounts for about 30 wt% of the total species on the SEI.

Mn deposition reaction on graphite

- Denying electrochemical reduction mechanism
  $Mn^{2+} + 2e \rightarrow Mn$
- Raise other possibility: Ion exchange model

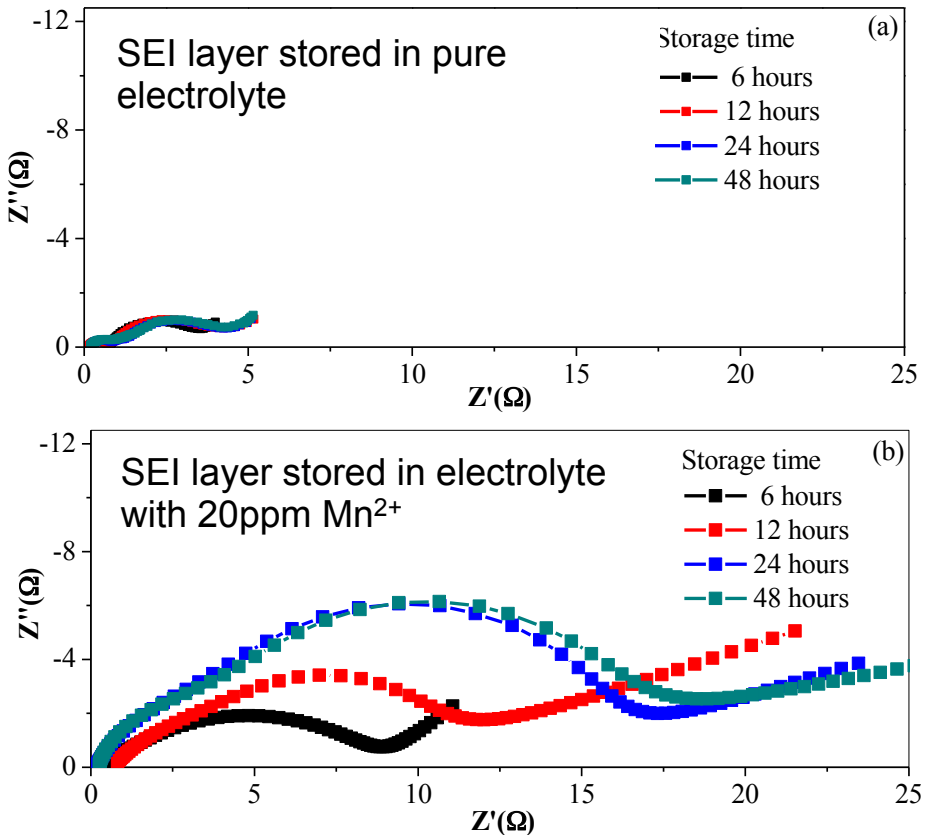


SEI layer stored in Mn^{2+}

Anodes	Mn concentration （ppm）	
	In pure electrolyte	In electrolyte with 20ppm Mn^{2+}
Fresh graphite without SEI	5.40	98.71
Cycled then fully lithiated graphite	4.81	131.63
Cycled then fully delithiated graphite	2.12	255.67

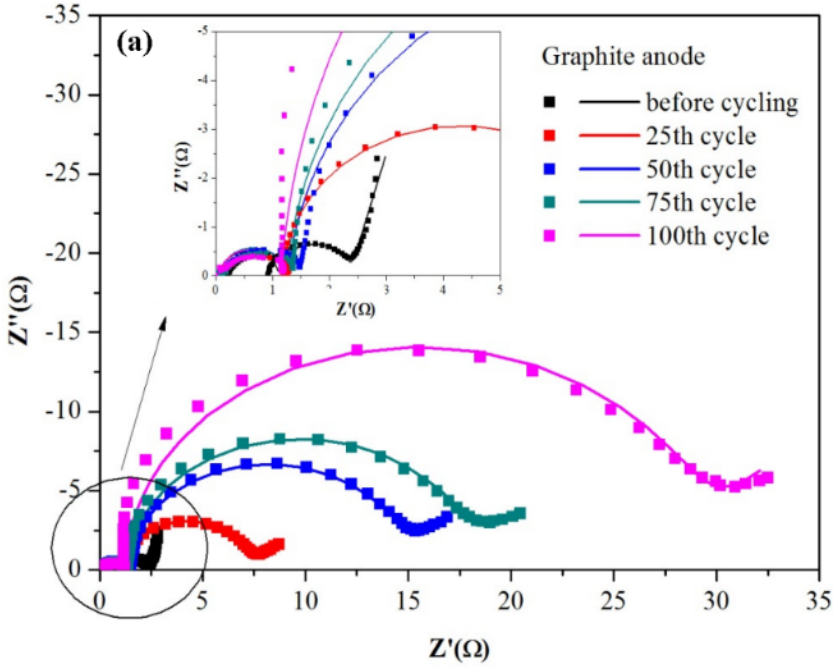
Ion-exchange and Impedance rising

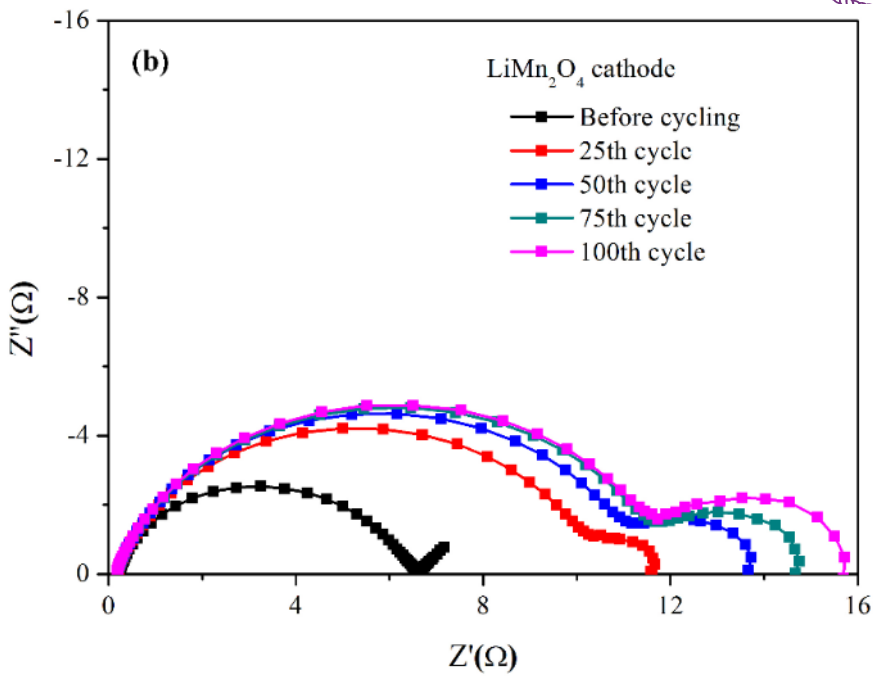
- The impedance rising of graphite anodes stored in an electrolyte with or without Mn^{2+}



- Mn^{2+} in the electrolyte reacts with the SEI on the graphite anode and modifies the nature of the SEI
- Impedance of graphite anode in the electrolyte with Mn^{2+} was stabilized after 24 hours, likely due to the depletion of Mn^{2+} in electrolyte

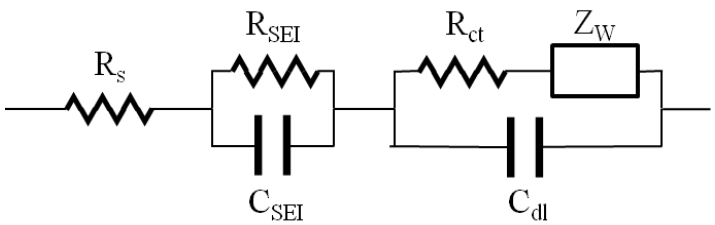
Impedance Measurements on Carbon Anode





- Three-electrode configuration applied to AC impedance measurement, allows to separate the cathode and anode.
- It appears that the impedance rise of the cathode is not responsible for the capacity loss.
- The trend of impedance rise from the anode matches that of the capacity loss during the cycle test, indicating that the anode impedance is the key factor that causes the capacity fading of the full cell.

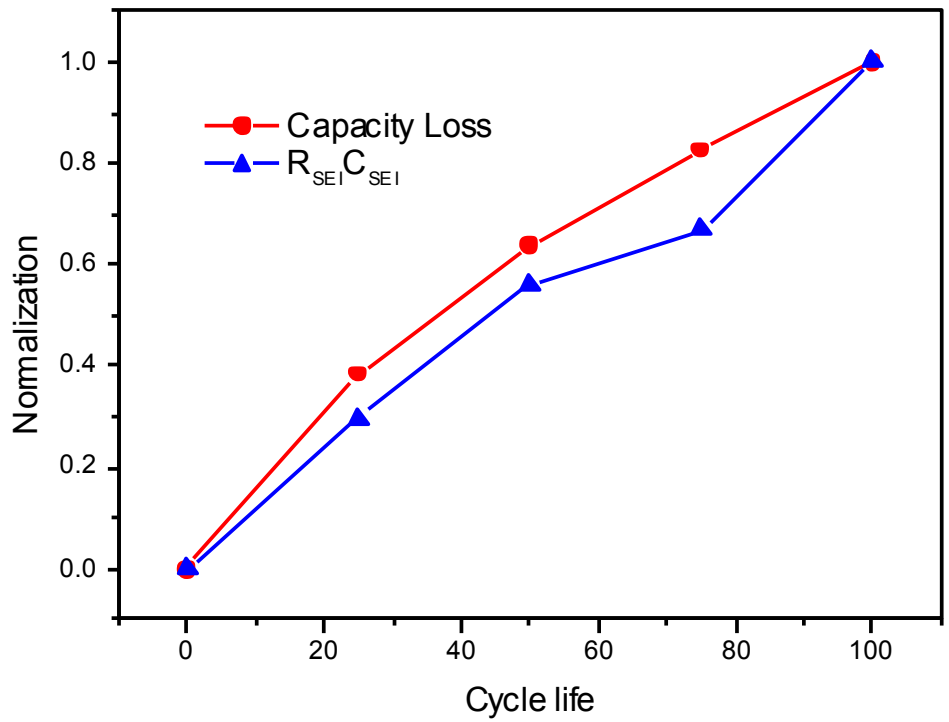
Capacity loss and degradation of SEI



$$R_{SEI} = \rho l / S$$

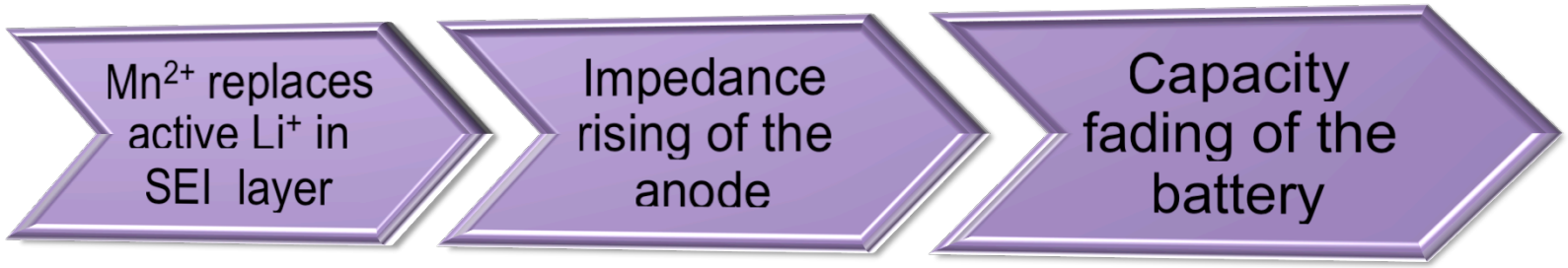
$$C_{SEI} = \varepsilon S / l$$

$$R_{SEI} C_{SEI} = \rho \varepsilon$$

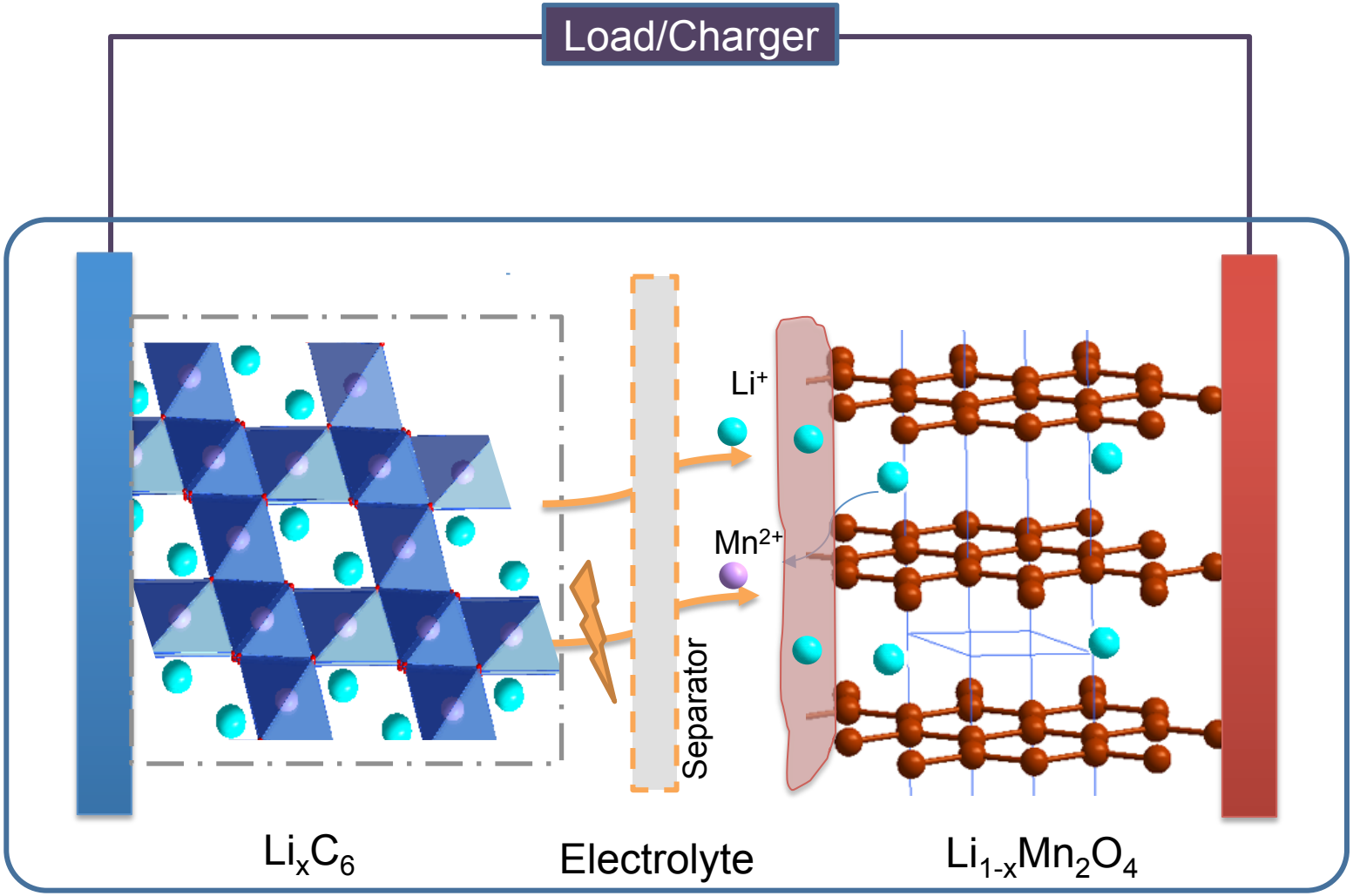


➢The capacity loss is well correlated with incensement in $R_{SEI}C_{SEI}$, which is induced by composition change of SEI layer due to the Mn deposition

Correlation between Mn deposition and capacity fading



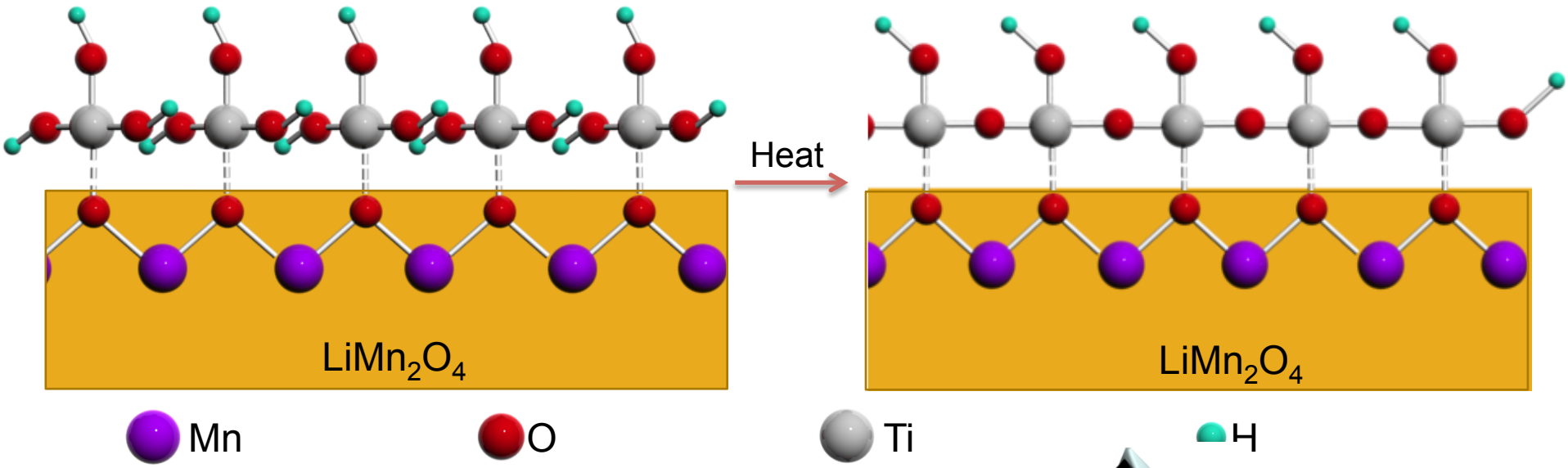
Suppression the dissolution the deposition by surface modification

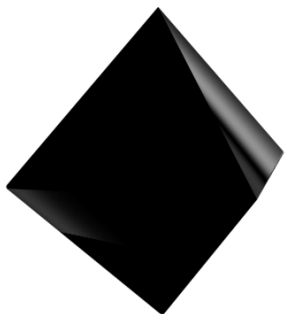


Surficial modified $LiMn_2O_4$

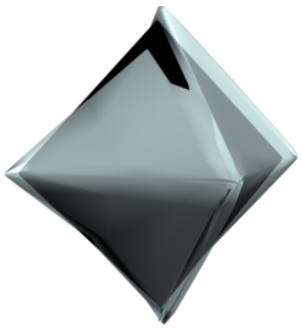
- Sol-gel method

$$Ti(OH)_4 + H^+ \rightarrow Ti(OH)_3^+ + H_2O$$



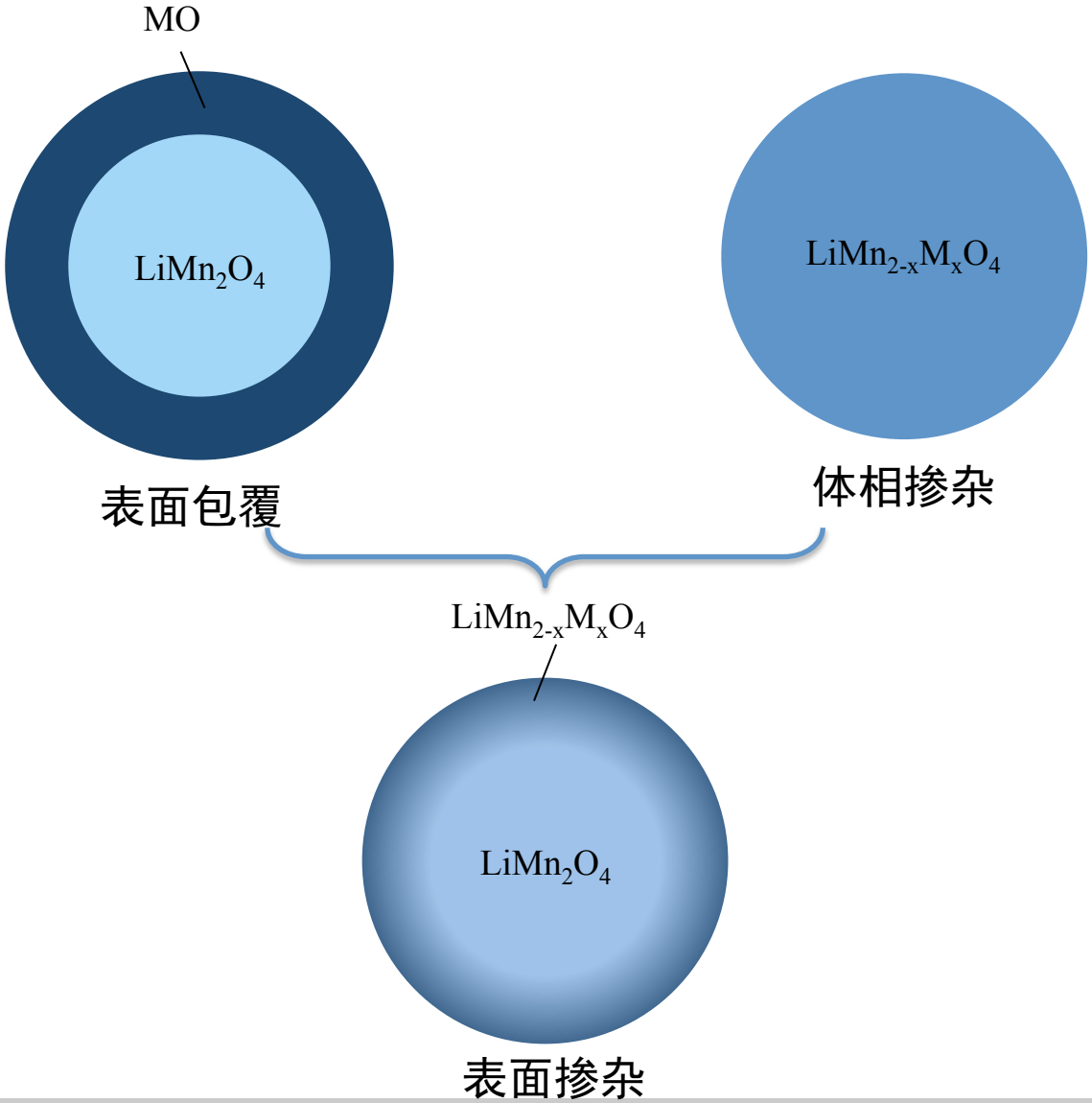


Bare $LiMn_2O_4$

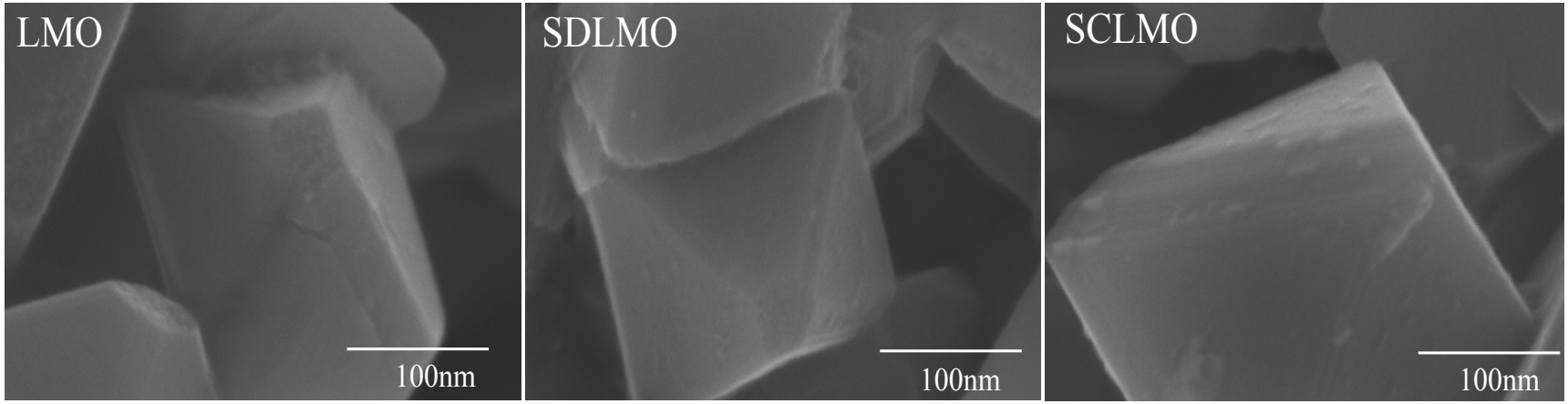


Surficial modified $LiMn_2O_4$

表面包覆、体相掺杂以及表面掺杂结构

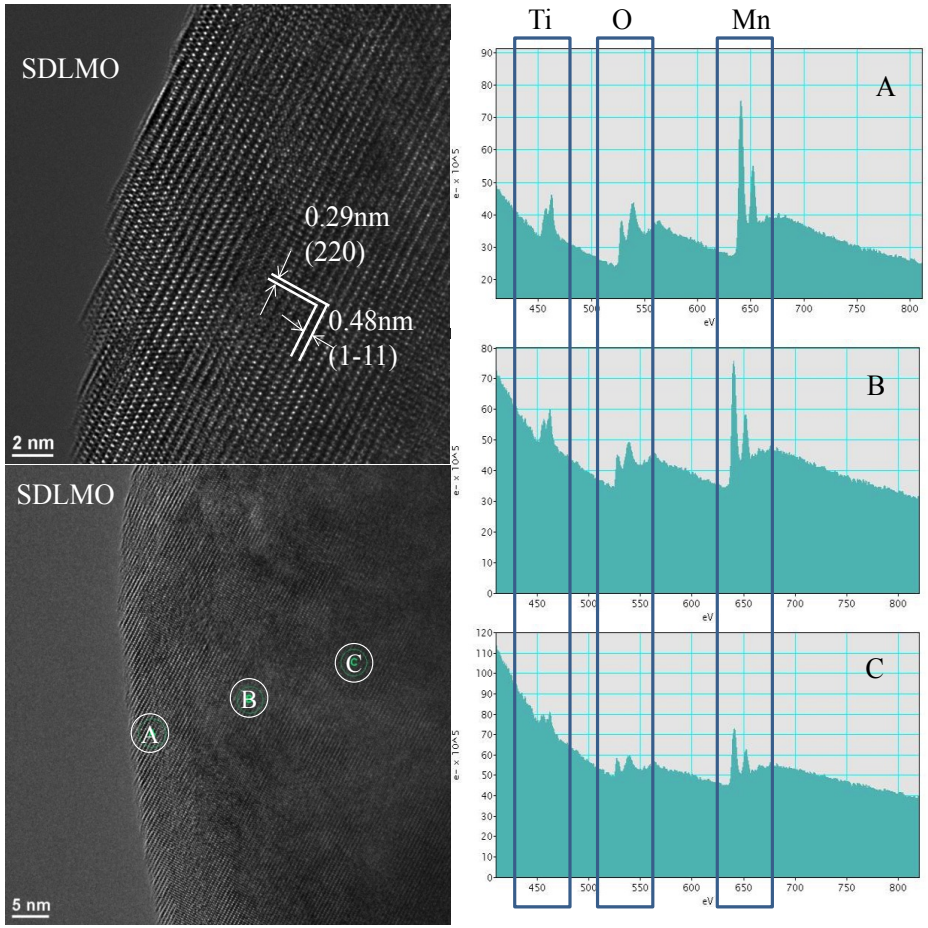


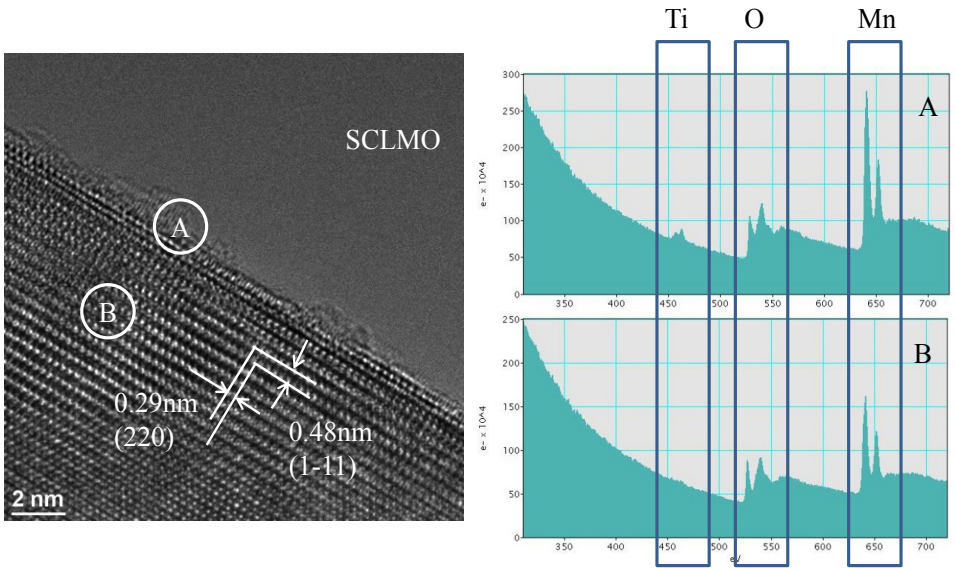
SEM images of particles



The smooth facets, particle size and octahedral morphology of the pristine LiMn2O4 particles were unchanged at the 100nm size scale after both the surface doping and ALD coating.

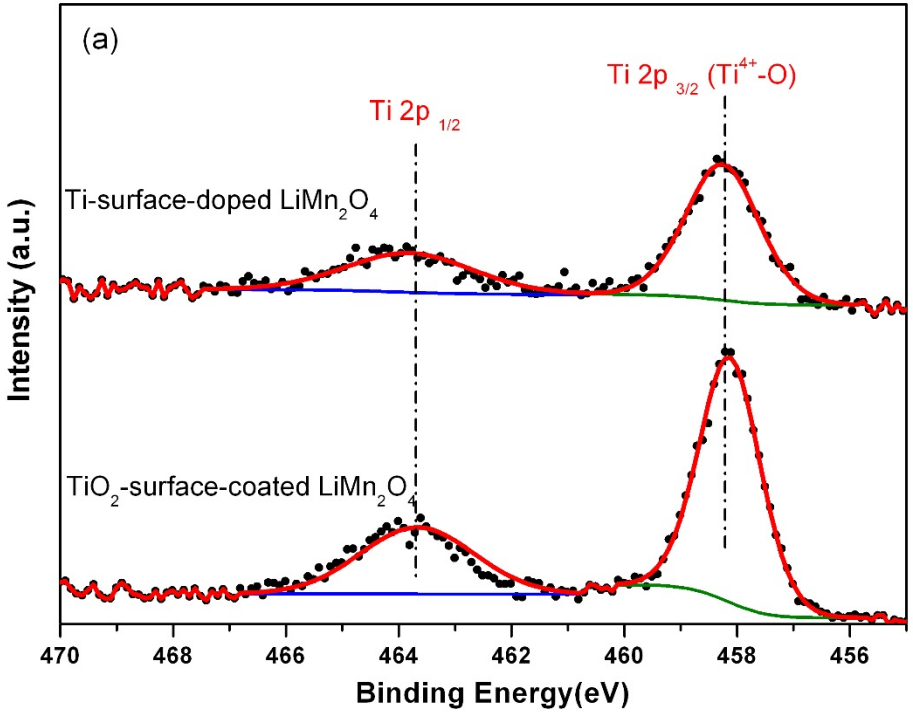
High resolution TEM images of surface treated LiMn2O4 particles



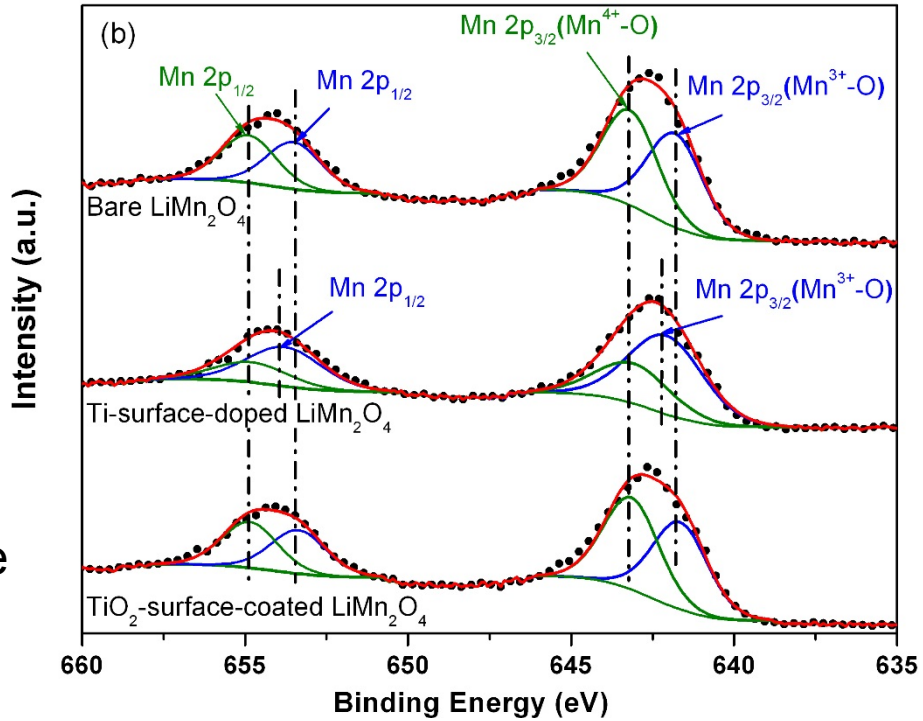


- SDLMO中检测到Ti元素，其体相和表层的晶格条纹没有明显变化，很可能由于Ti进入了锰酸锂的晶格形成了具有尖晶石结构的掺杂层。
- 在SCLMO中，Ti只能在颗粒表面区域检测到，而且表层观察到约为1-2nm的岛状颗粒。

表面改性锰酸锂的表面分析（XPS）

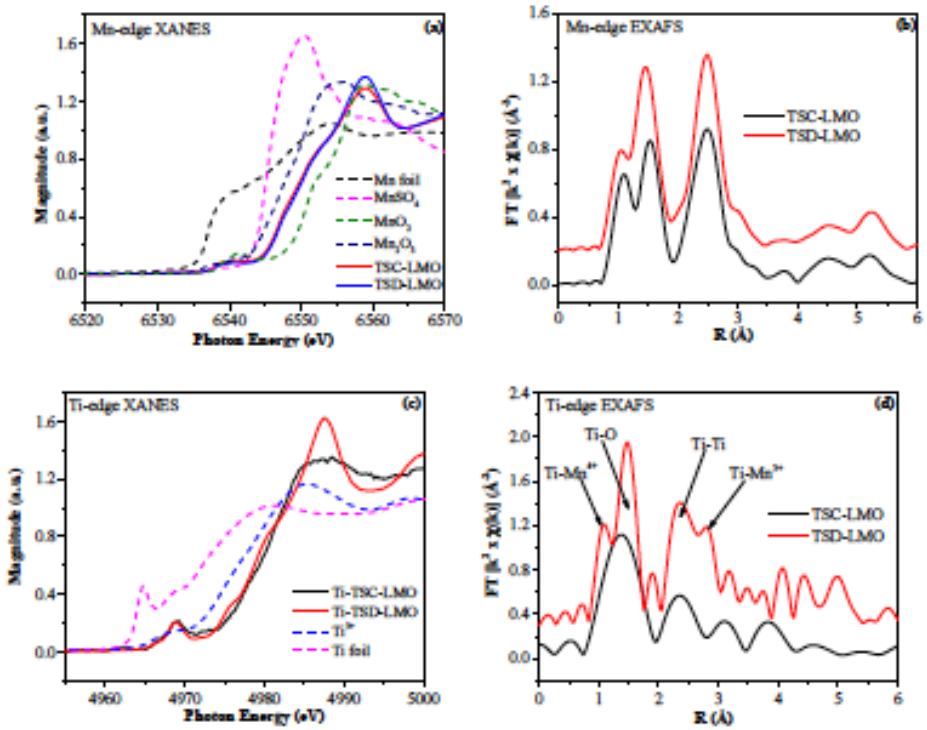


- 表面包覆和表面掺杂的锰酸锂表面的Ti以Ti（IV）形式的存在



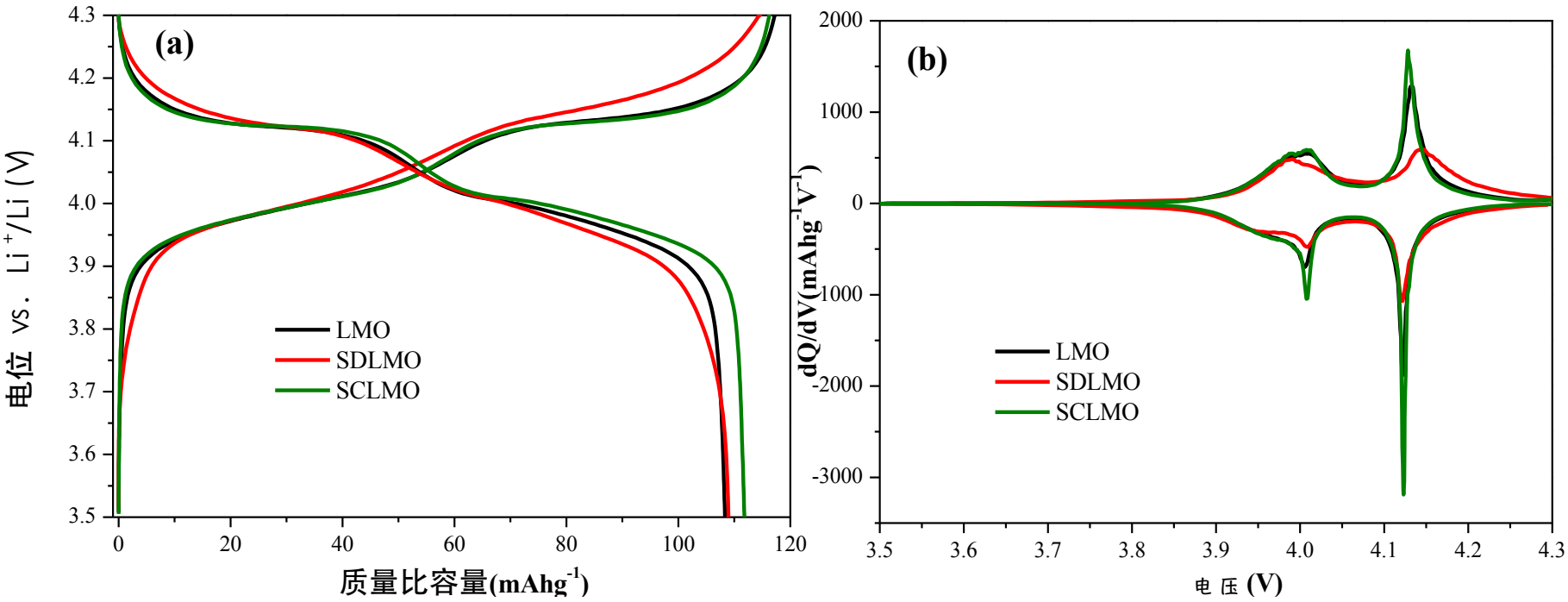
The bulk crystal structure of spinel LiMn2O4 is not affected by the surface modifications.

X-ray absorption spectroscopy



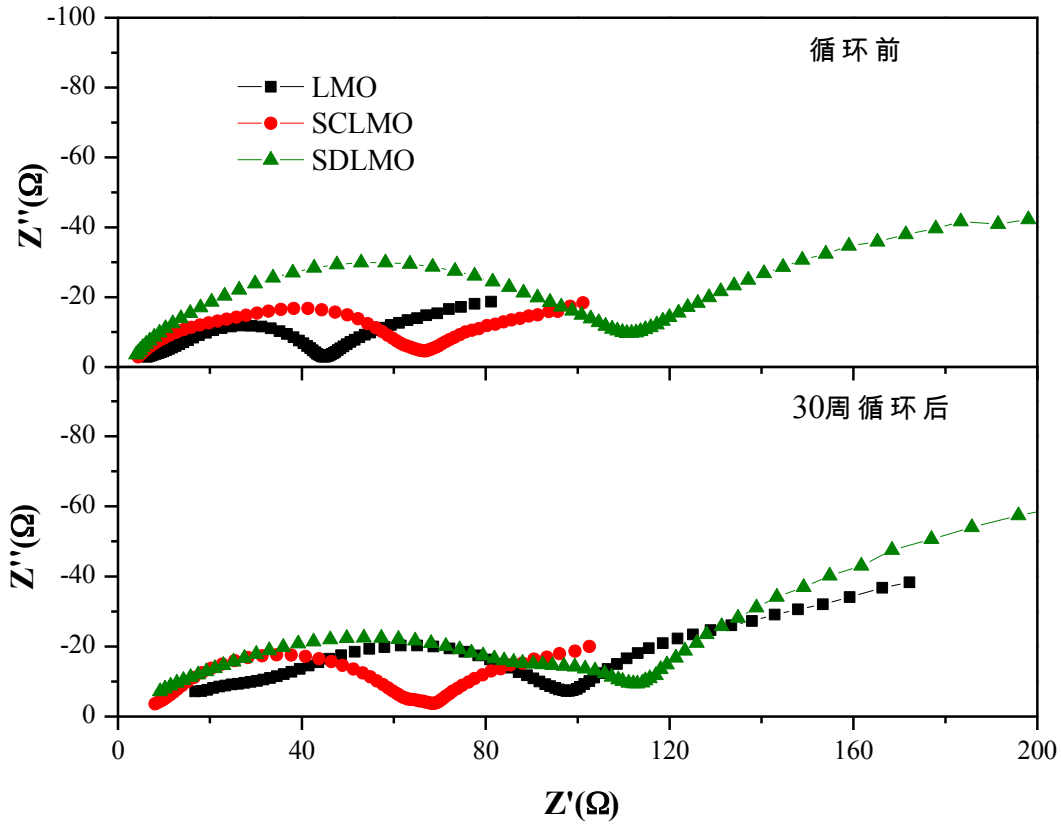
- Both surface-modified LiMn2O4 samples exhibit nearly identical features as the pristine LiMn2O4 in XANES and EXAFS of Mn K-edge, suggesting that the bulk crystal structure of spinel LiMn2O4 is not affected by the surface modifications.
- In Ti K-edge x-adsorption spectra, two extra bonding features are also observed, likely due to theinteractions between Ti and Mn(IV/III) in the TSD-LMO sample (i.e. Ti-Mn4+ and Ti-Mn3+).

The charge-discharge curves



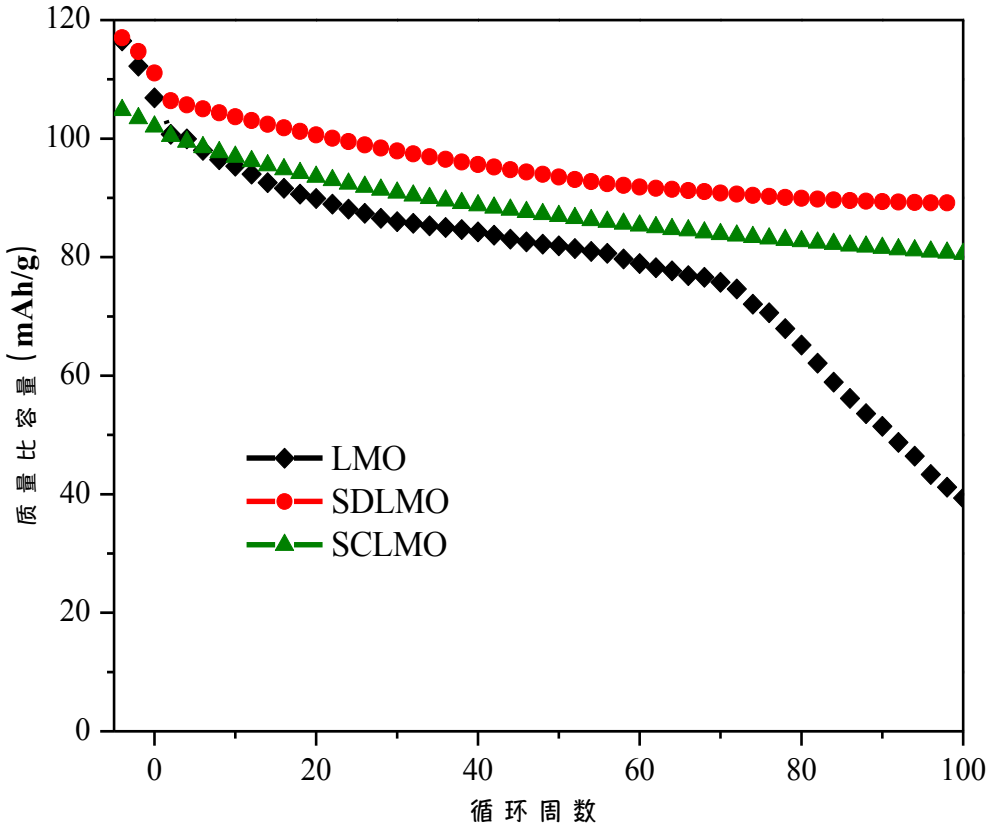
- The oxidation peak at around 4.1V was significantly broadened in the TSD-LMO electrode, which is likely due to the formation of a LiMn2-xTixO4 layer on the surface of the LiMn2O4 particles .
- The initial columbic efficiencies of the TSD-LMO and TSC-LMO (94.9% and 96.1%, respectively) are higher than that of the pristine LMO (92.3%)

电化学阻抗谱测试



- 表面改性会增大锰酸锂表面的电荷传输电阻，但是SDLMO的电化学阻抗小于SCLMO
- LMO的电化学阻抗在高温循环后增大，SDLMO和SCLMO电化学阻抗在循环前后基本不变，表明通过表面改性可以有效的提高锰酸锂的表面稳定性

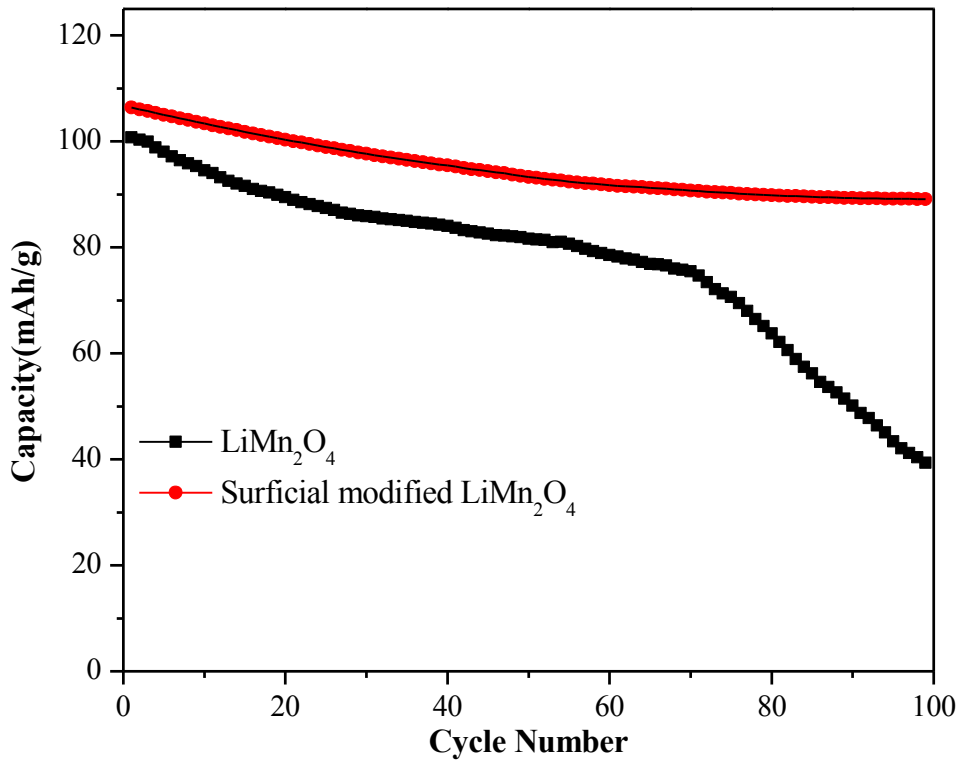
高温循环性能测试和溶解-沉积过程

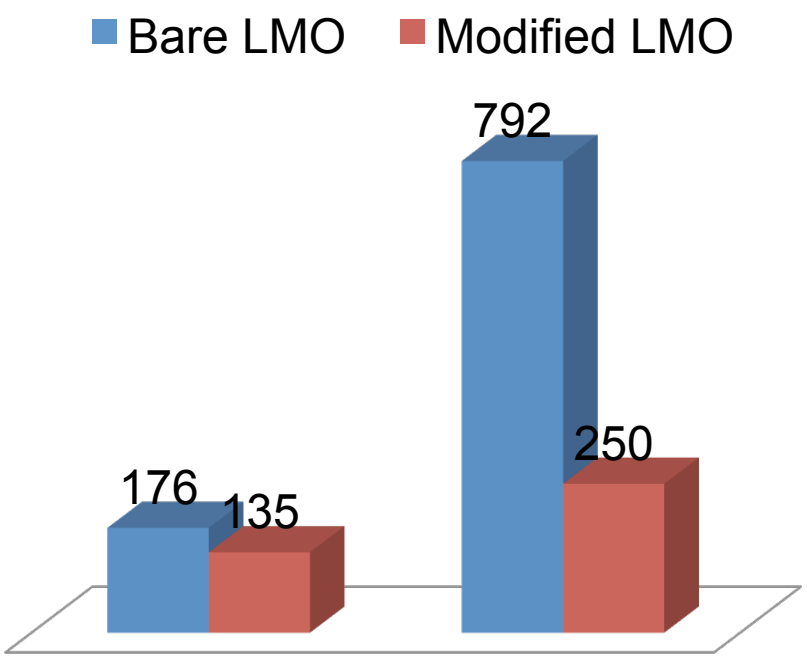


样品	电解质中Mn的浓度 (ppm)	循环后负极中Mn的浓度 (ppm)
LMO	176	792
SDLMO	135	250
SCLMO	93	263

- 表面包覆和表面掺杂提高了锰酸锂的表面稳定性，有效抑制了锰酸锂在电解质中的溶解，并因此抑制了Mn在负极的沉积过程，从而提高了锰酸锂的高温循环性能。

Comparison of

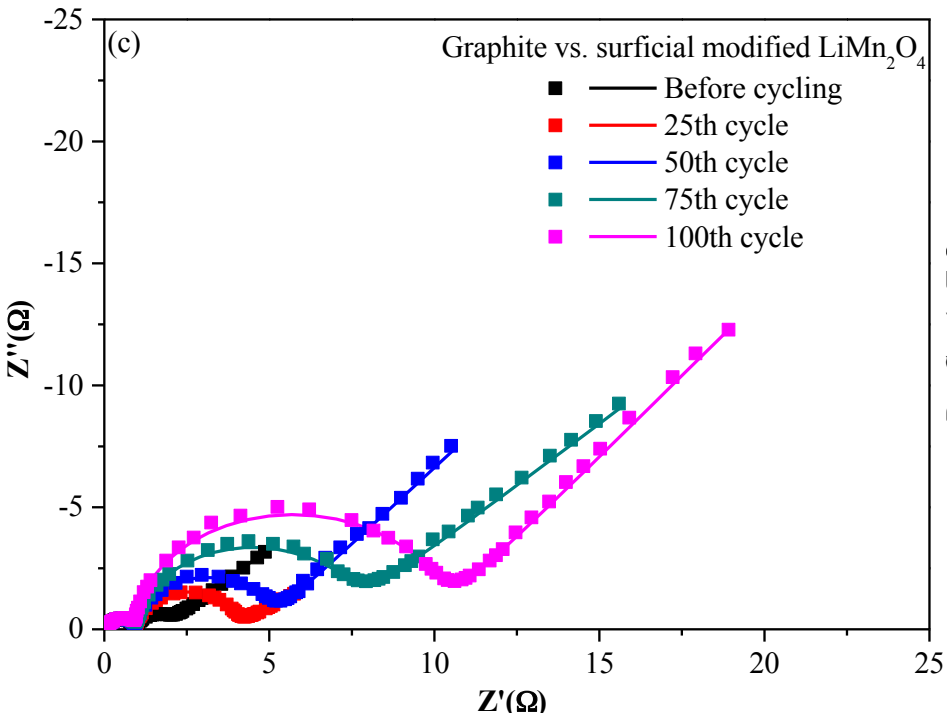


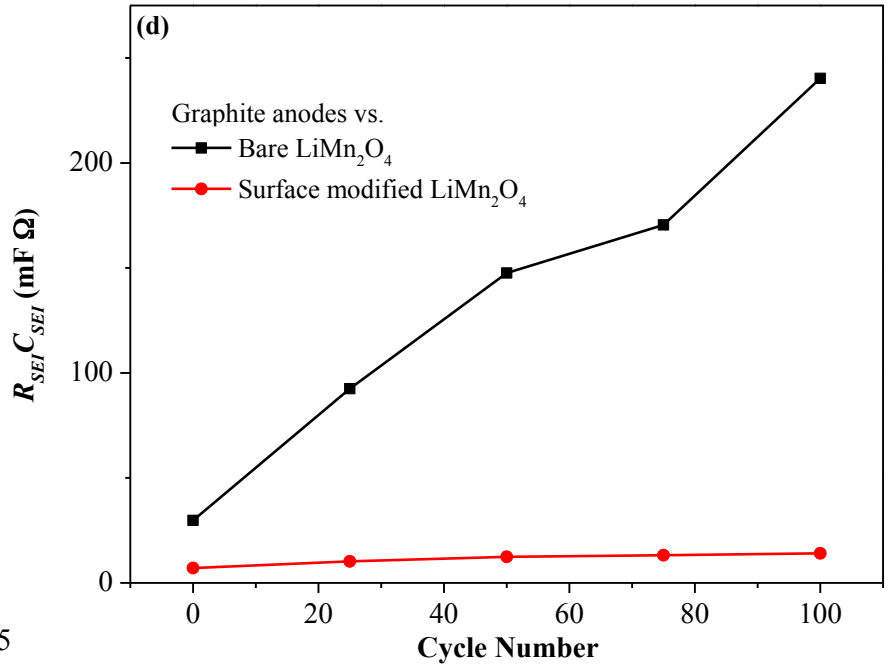


Mn concentration in electrolyte after storage at 55°C (ppm)

Mn concentration on anode after cycling at 55°C (ppm)

Impedance of anodes from modified systems

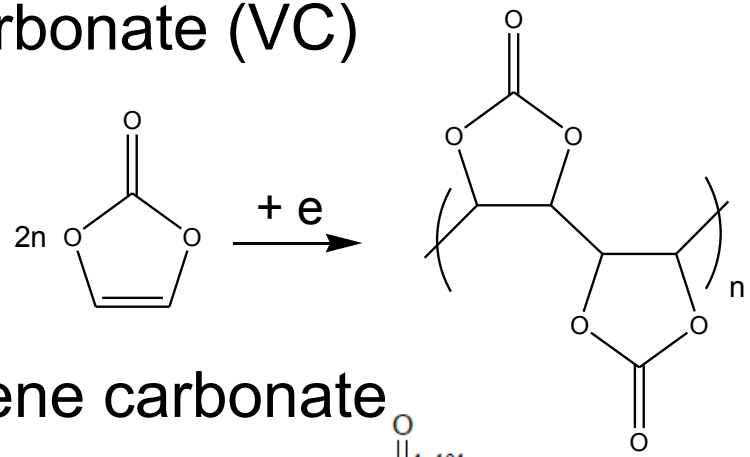




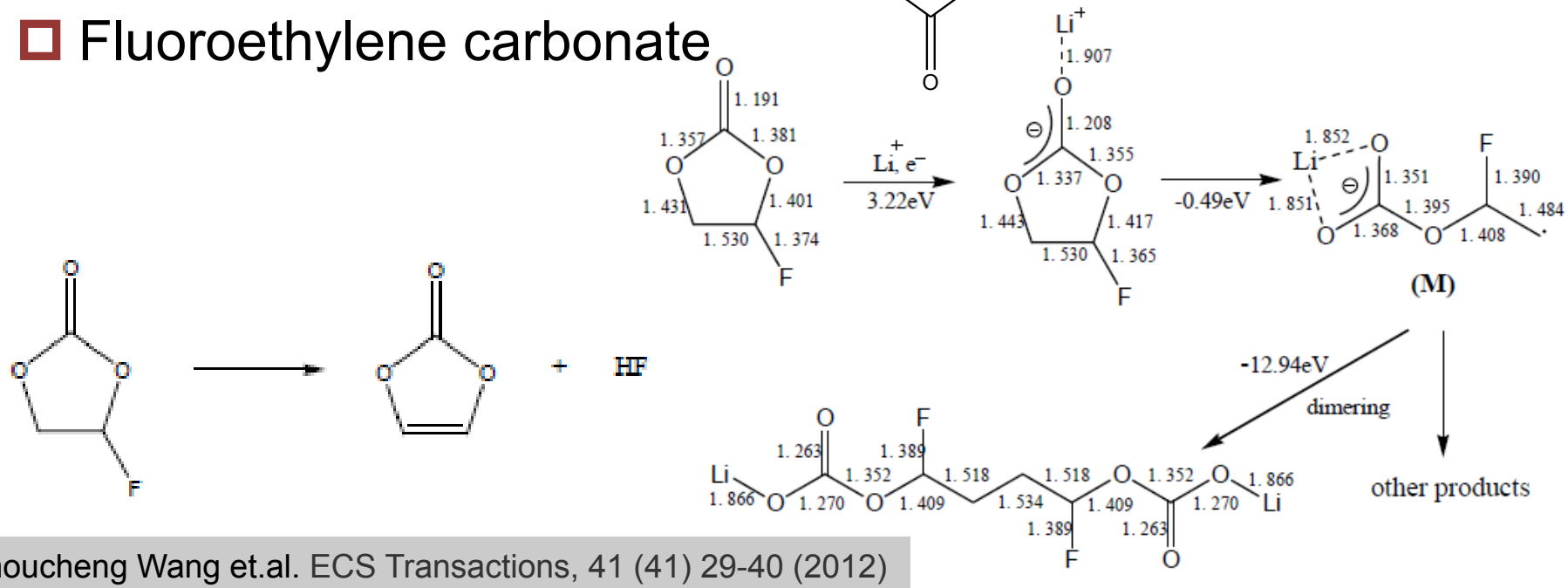
- The concentration of Mn deposition on anode was reduced from 700ppm to 250ppm by surficial modification.
- Further confirm that the capacity fading is caused by changes in the SEI on the graphite anode due to the Mn^2 migrated from the cathode, and thus the change of the impedance of the graphite anode

Commonly used electrolyte additives

- Vinylene carbonate (VC)

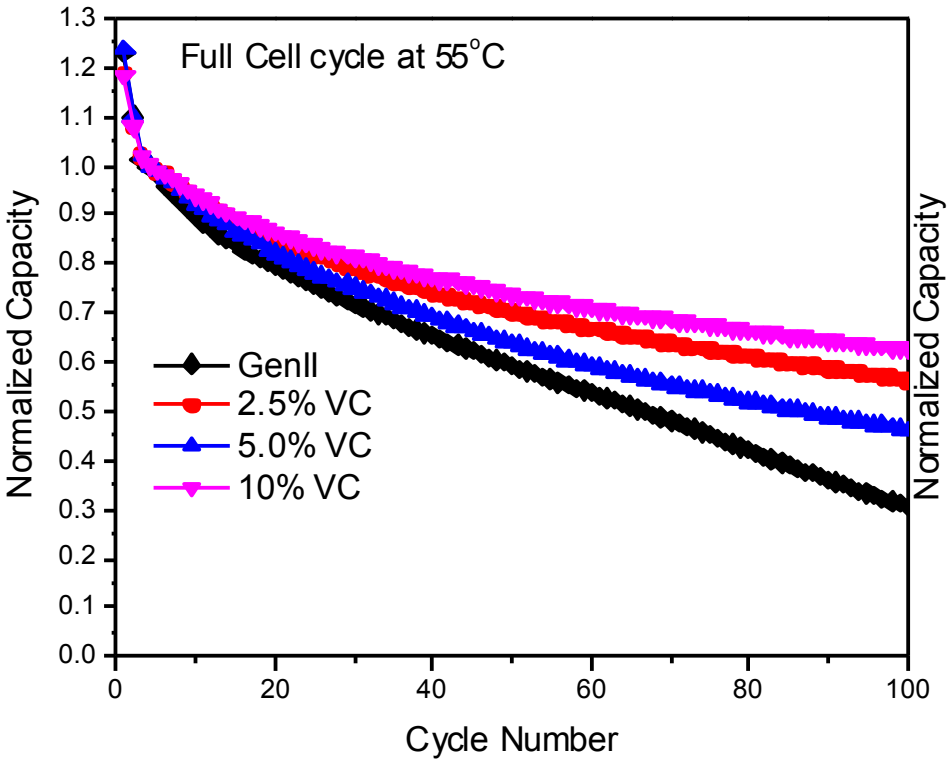


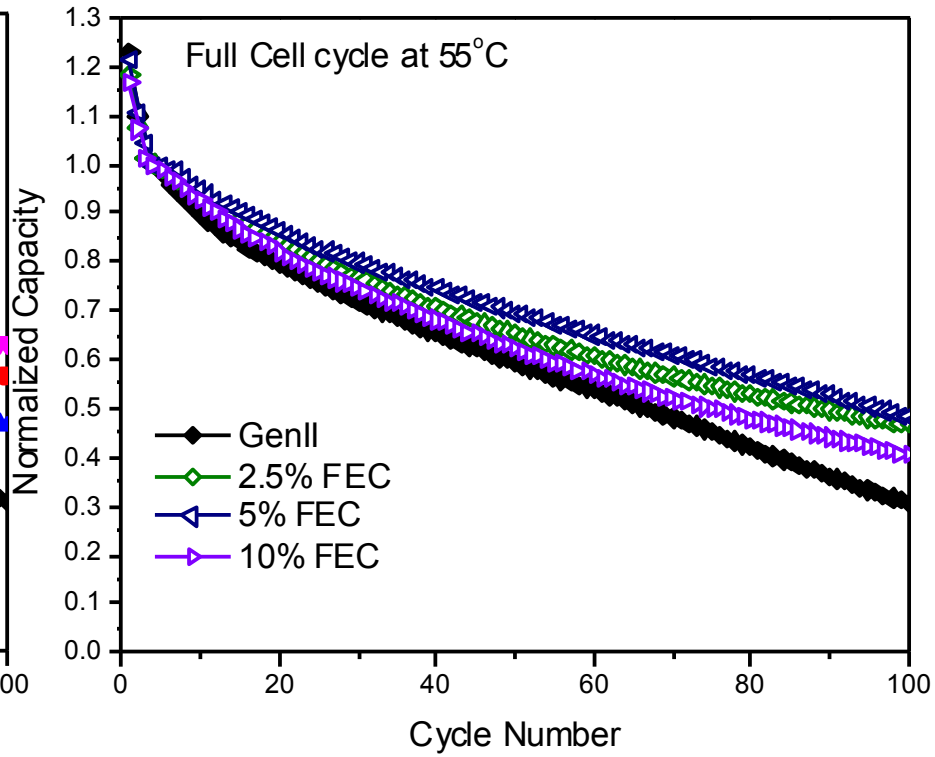
- Fluoroethylene carbonate



Zhoucheng Wang et.al. ECS Transactions, 41 (41) 29-40 (2012)
Zhang, S. S *J. Power Sources* **162**, 1379-1394 (2006).

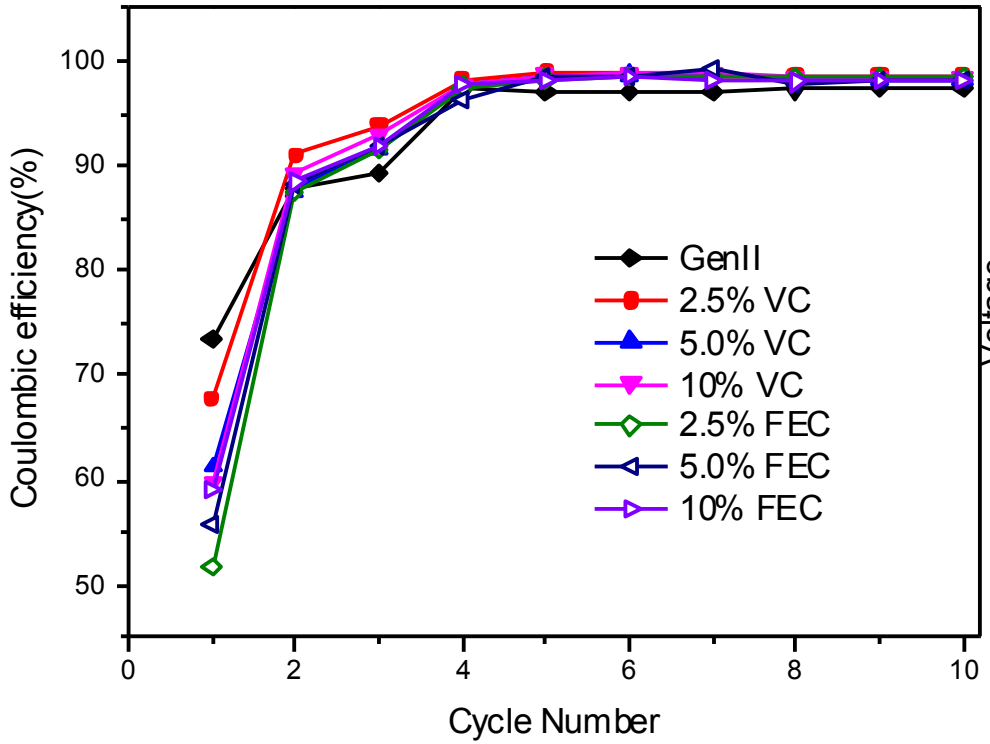
Cycle performance @ 55°C

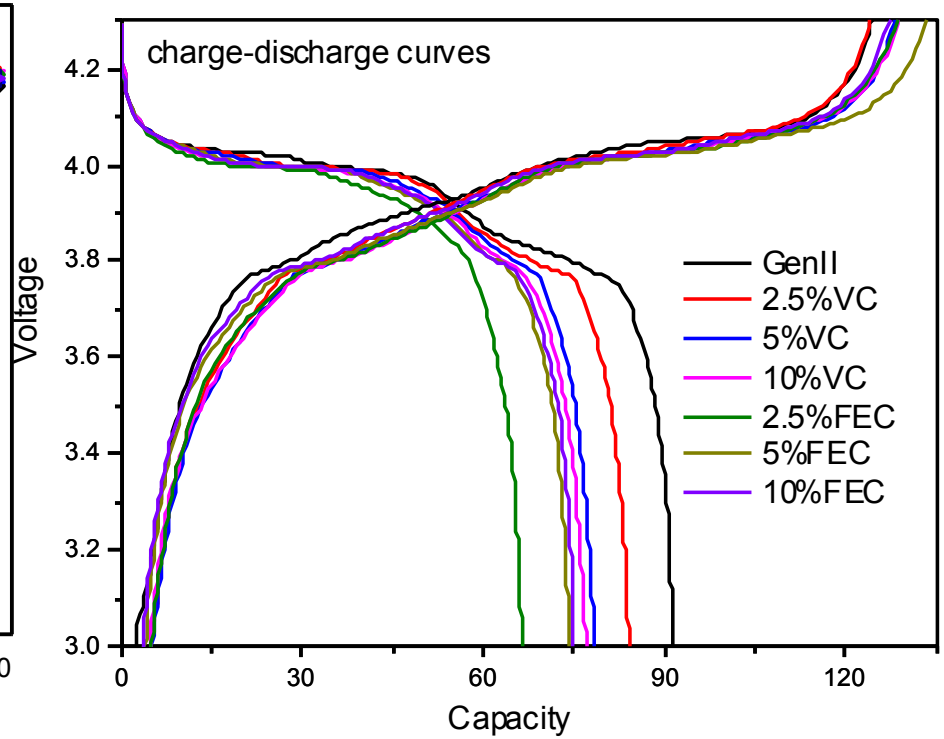




➢The cell with 10% VC in GenII as the electrolyte shows the best cycle performance.

Coulombic efficiency





➢The initial coulombic efficiency was decreased by additives, due to the irreversible reactions induced by the additives.

Mn deposition on MCMB after cycling(ICP-AAS)

Sample #	Label	Mn concentration(ppm)	Description
1	GenII	860.62	MCMB anodes were cycled against $LiMn_2O_4$ cathodes in different electrolytes at 55°C for 100 cycles.
2	2.5VC	1032.65	
3	5VC	1144.96	
4	10VC	1222.52	
5	2.5FEC	1359.37	
6	5FEC	1336.10	
7	10FEC	1488.17	

➢The concentration of Mn is not decreased by VC or FEC

Ion-exchange reaction between Mn^{2+} and SEI

Sample #	Label	Mn concentration(ppm)	Description
1	GenII in Mn	455.79	MCMC anodes were cycled in different electrolytes for 25 cycles to form the SEI layers, then stored in electrolyte with Mn^{2+} for 7 days
2	2.5VC in Mn	478.46	
3	5VC in Mn	483.79	
4	10VC in Mn	523.96	
5	2.5FEC in Mn	514.93	
6	5FEC in Mn	605.83	
7	10FEC in Mn	662.32	

➢The ion-exchange reaction is not suppressed by VC or FEC

Summary

- The oxidation state of manganese deposited on the anodes is +2 by XAS and XPS analysis.

- A metathesis reaction between Mn^{2+} and some species on the SEI during the deposition of Mn on the anodes, rather than a reduction reaction that leads to the formation of metallic Mn otherwise, as speculated in earlier studies.

- The capacity fading is caused by changing of the SEI on the graphite anode due to the continuous reaction with the dissolved Mn^{2+} from the cathode.

Thanks for your attention!

Acknowledgements

Authors State Key Basic Research Program of PRC (2009CB220105), Beijing Natural Science Foundation (2120001)National International Science and Technology Cooperation Project (2012DFG61480), Vehicle Project (2011AA11A290), China-US Electric Vehicle Project (2010DFA72760),.