

Transmission Electron Microscopy as a Powerful Tool for Investigating Lithium-ion Battery Materials

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ABSTRACT Transmission electron microscopy (TEM) stands out as one of the most powerful tools for characterizing materials at multiple scales and dimensions. This unique technique has nowadays been widely employed in investigating the lithium-ion battery (LIB) materials. The present perspective paper focuses on several LIB related aspects that are recently revealed by using TEM. Finally, we present outlook on the future directions of TEM for LIB research and development.

Keywords: transmission electron microscopy, lithium-ion batteries, structures, properties;

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As a booming clean energy, rechargeable lithium-ion batteries (LIBs) have already attracted broad attention and recently been awarded the Nobel Prize in chemistry^[1]. The electrochemical performances of LIBs are highly relevant to both the surface and bulk structures of the electrodes, *e.g.*, the solid electrolyte interphase (SEI) contributes effectively to the cycle stability while the electrode phase is dominant for the LIB capacity^[2]. Thus revealing the structural features of these phases is of particular significance for both theoretical studies and practical applications. Characterization techniques like X-ray diffraction (XRD) or neutron diffraction (ND) and X-ray adsorption spectroscopy (XAS) can respectively offer the crystallographic information and probe the chemical environment and electronic structures. However, they all suffer from the limitations of low spatial resolution. In contrast, advanced transmission electron microscopy (TEM) is a very powerful tool for probing material structures with much higher spatial resolution^[3]. Furthermore, TEM could not

only provide the structural information *via* high angle annular dark field (HAADF) image or electron diffraction (ED), but also yield elementary composition, electronic structure, and coordination environment when combined with energy dispersive X-ray spectrometer (EDX) and electron energy loss spectrometer (EELS) (Fig. 1)^[4]. These have also made TEM a very versatile tool in characterizing materials at multiple scales. Due to its superior capability, TEM has therefore been widely used to probe the structural and chemical information of LIBs and their correlation with the electrochemical performances.

The interface of the active solid electrode towards the liquid electrolyte is the place that a fairly complex reaction occurs, causing the formation of the well-known SEI and the structural rearrangement in the surface of the electrode materials, which are much difficult to probe by XRD or XAS techniques due to the nanoscale thickness. Fortunately, these structural variations could be easily captured by the

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TEM characterizations. The transformation to rock-salt phase in the surface of the layered oxide cathode upon cycling is a common phenomenon limiting the long-term electrochemical performance. By the scanning transmission electron microscopy (STEM) HAADF analysis, it is found that the stepped (002) and (111) configurations of the transformed rock-salt phase are derived from the (01 $\bar{4}$) and (003) surfaces of the original layered $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ structure. These reconstructed surfaces are adverse to the stable electrochemistry

due to their reduced ionic and electronic conductivity of the cathode^[5]. Furthermore, the layered to rock-salt phase transformation on the particle surface can also affect the bulk lattice behavior of the electrode. In the Ni rich $\text{LiNi}_{0.76}\text{Co}_{0.10}\text{Mn}_{0.14}\text{O}_2$ (NCM76) cathode, STEM-HAADF images revealed that such a transformation could lead to an anisotropic bulk growth traversing the fast Li diffusion channels, which was controlled by the solid-liquid interfacial reaction (Fig. 2a)^[6].

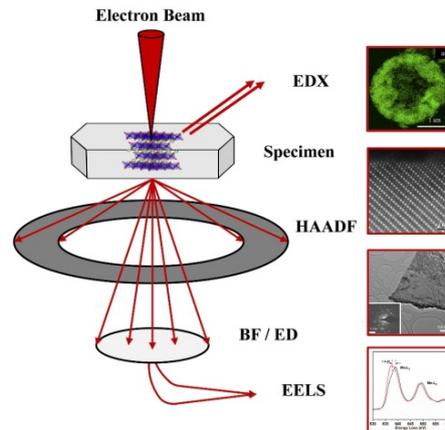


Fig. 1. Schematic representation of TEM techniques in LIB researches. Reproduced from references [4], [9], [10] and [12]

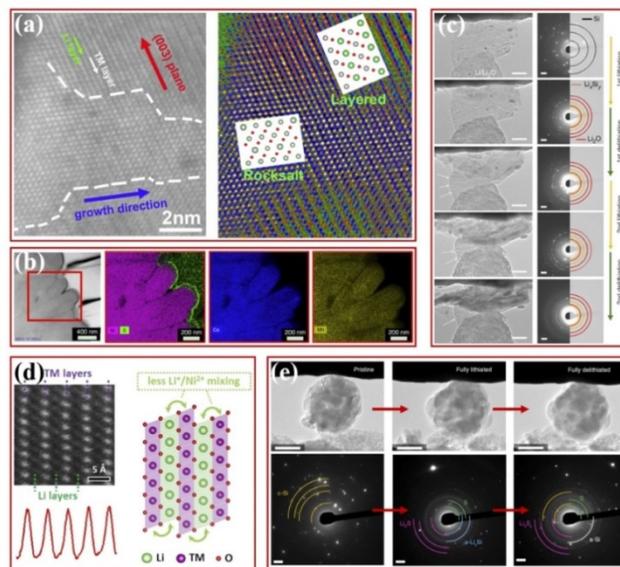


Fig. 2. TEM applications in the interfaces and compositions of LIB field. (a) Anisotropic bulk growth of the layered to rock-salt phase transformation. (b) EDX mapping of the PEDOT deposited NCM111 particles. (c) *In situ* TEM with ED of the amorphous carbon coated Si nanosheets upon cycling. (d) Mo doping hinders the $\text{Li}^+/\text{Ni}^{2+}$ mixing. (e) *In situ* TEM with ED of the S doped Si particles upon cycling. Reproduced from references [6], [8], [9], [10], and [12]

Surface modification of the electrode has been validated as a widely deployed strategy to alleviate the electrode reactivity with electrolyte, which are

observable by TEM imaging^[7]. For instance, an oxidative chemical vapour deposition (oCVD) method was employed to build an electronically

conductive and ionically permeable poly(3,4-ethylenedioxythiophene) (PEDOT) skin on the $\text{LiNi}_{0.80}\text{Co}_{0.10}\text{Mn}_{0.10}\text{O}_2$ (NCM811) cathode. TEM imaging together with EDX mapping can be used to identify the ultraconformal protective layer on both the secondary and primary particles, which remained integrated after cycling for an enhanced electrochemical performance (Fig. 2b)^[8]. For the potential Si anode with a large volume change, a 2D Si nanosheet coated with amorphous carbon layers was developed. *In situ* TEM experiment was used to reveal an unusual swelling/deswelling mechanism, which is responsible for releasing the cycling induced stress to maintain the structural and interfacial stability (Fig. 2c)^[9].

TEM is also used for studying the electrode compositions and their effects on electrochemical performance. To improve the electrode properties, doping is one of the most successful methods. It is observed by TEM and EDX that minor uniform Mo doping in the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode can hinder the $\text{Li}^+/\text{Ni}^{2+}$ mixing, which further suppresses the detrimental phase transformation for an enhanced cycling stability (Fig. 2d)^[10]. Al is another commonly doped element in the layered oxide cathode, and the TEM image analysis uncovered that Al could exist uniformly in the bulk lattice and as aluminum oxide nano-islands near the particle surface to lower the transition metal redox energy level^[11]. The doping strategy is also viable for anode. For example, *in situ* TEM verified that trace S doping in Si particle could minimize the volume change during cycling. Further, the phases formed in the lithiation/delithiation process could also be analyzed by ED (2e)^[12].

Electrolyte is another very important factor that has severe influence on the LIB performances, which can also be evaluated by the TEM technique. Zhang *et al* developed a novel electrolyte based on the fluorinated orthoformate solvent, which was beneficial for both the cathode and anode. TEM-based cryo-electron microscopy (cryo-EM) image indicated the formation of the uniform, stable, and amorphous SEI on the Li anode, which can efficiently reduce the pulverization and depletion of

Li. In addition, this new electrolyte can also strongly suppress the layered to rock-salt phase transformation of the NCM811 cathode, as proved from the high-resolution TEM images (Fig. 3a)^[13]. Another high-concentration ether electrolyte for high voltage (> 4.3 V) LIBs has recently been exploited and TEM results suggested that this electrolyte conducted to the stable CEI to preserve the structural integrity of the Ni-rich cathode under 4.5 V high cut-off voltage, demonstrating the effect of the electrolyte on cathode stability^[14]. Besides the solvent, various additives also exhibit obvious impact on the electrode properties. Taking lithium bis(oxalato)borate (LiBOB) as an example, STEM-HAADF imaging indicated the absence of the rock-salt phase on the NCM76 surface when LiBOB was added to form a compact CEI layer, which could significantly alleviate the oxidation of both the solvent and LiPF_6 and suppress the $\text{Li}^+/\text{Ni}^{2+}$ mixing (Fig. 3b)^[15].

TEM can also be utilized to assess the impact of other factors on the properties of electrode. For instance, the cycling rate can alter the phase transition pathway in the Ni-rich cathode. It was found by the STEM-HAADF imaging that the rock-salt phase was preferred under low cycling rate (1C) due to the thorough $\text{Li}^+/\text{Ni}^{2+}$ mixing induced by the sufficient Li vacancies, while the spinel structure was favored at a high cycling rate (2C) owing to the impeded Ni migration arising from the Li retention (Fig. 3c)^[16].

The electrode behavior can be altered by *in situ* TEM to study the delithiated $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NCM622) cathode upon thermal perturbation and found the explosive nucleation and propagation of the intragranular cracks. The thermal stress accompanied by the electrochemically induced phase inhomogeneity and internal pressure from the oxygen release took the main responsibility for such a behavior^[17]. Moreover, thermal treatment of the cathode can also trigger the phase evolution. By *in situ* TEM technique, it was unfolded that the Li/O loss at the surface of a Ni-rich cathode ($\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$) was accelerated at high temperatures and finally caused the unusual bulk-to-surface transformation from the layered to rock-salt phase (Fig. 3d)^[18].

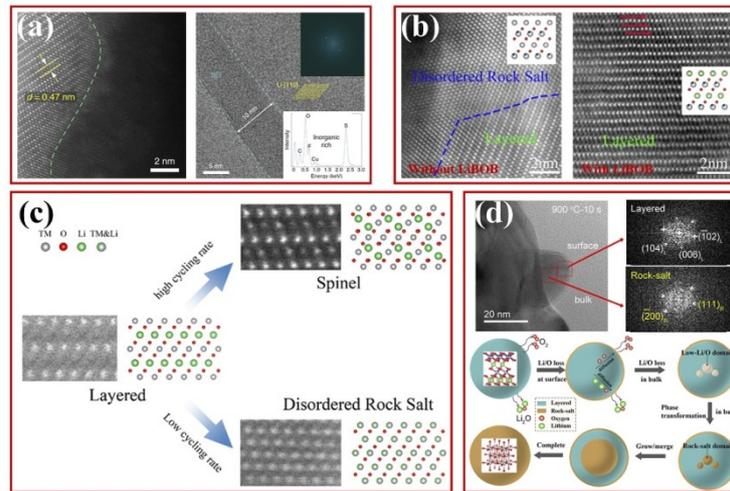


Fig. 3. TEM applications in the electrolytes and other aspects of LIB field. (a) The structures of NCM811 cathode and Li anode after cycling with the electrolyte based on the fluorinated orthoformate solvent. (b) STEM-HAADF images of the NCM76 without and with the LiBOB additive. (c) Cycling rate induced different phase transformation for the Ni-rich cathode. (d) *In situ* TEM detection of the unusual bulk-to-surface transformation from the layered to rock-salt phase. Reproduced from references [13], [15], [16], and [18]

In summary, the advanced TEM technique has been broadly employed in the research and development of LIB due to its high spatial/temporal resolution and versatile capability for systematic studies on both the crystalline and amorphous phases including the atomic structures, compositions, and electronic structures. Many aspects concerning the LIB performances such as interfaces, compositions, electrolytes, and electrochemical process have already been investigated by this powerful tool to obtain numerous achievements. Some of the future development directions for the TEM studies of LIB materials can be addressed herein as follows. (1) Minimizing the electron beam damage on the samples to avoid possible artifacts. Feasible approaches include reducing the beam dose rate and total dose, which results in the poor signal to noise ratio and therefore likely compromises image resolution. Cryo-EM and more advanced detectors with higher sensitivity represent other viable approaches to alleviate the sample damage. (2) Although the heavy transition metal atoms can be directly detected by the STEM-HAADF imaging, it still remains a great challenge as to acquire the information of light atoms like oxygen and even

lithium. Developing new imaging method, such as annular bright field (ABF) imaging, for direct quantification of light atoms is significant, especially for the Li charge carrier. (3) Exploiting *in situ* electrochemical cycling methods and capabilities integrated in the TEM instruments^[19]. This is another very large challenge due to the difficulty in constructing the microbattery in the TEM vacuum condition. Although very few studies have reported *in situ* TEM electrochemical experiments, the battery architectures are quite different from the practical ones, and the electrochemistry quantification at nanoscale is another severe problem for hindering the exploitation^[20]. (4) Applying ED for more specific structural analysis. Compared with the imaging mode in the LIB researches, less attention is paid to the ED method, which has been proved as a very powerful tool for characterizing the crystalline structures. Moreover, the recently developed 3D ED techniques like continuous rotation electron diffraction (cRED) on nano crystals have not been introduced to the LIB area, which may unveil more valuable insights into the structure-property relationship of LIB materials^[21].

REFERENCES

- (1) Castelvechi, D.; Stoye, E. Chemistry Nobel honours world-changing batteries. *Nature* **2019**, 574, doi: 10.1038/d41586-019-02965-y.
- (2) Fan, X. L.; Ji, X.; Han, F. D.; Yue, J.; Chen, J.; Chen, L.; Deng, T.; Jiang, J. J.; Wang, C. S. Fluorinated solid electrolyte interphase enables highly reversible solid-state Li metal battery. *Sci. Adv.* **2018**, 4, eaau9245.
- (3) Qian, D. N.; Ma, C.; More, K. L.; Meng, Y. S.; Chi, M. F. Advanced analytical electron microscopy for lithium-ion battery. *NPG Asia Mater.* **2015**, 7, e193.
- (4) Liu, T. C.; Dai, A.; Lu, J.; Yuan, Y. F.; Xiao, Y. G.; Yu, L.; Li, M.; Gim, J.; Ma, L.; Liu, J. J.; Zhan, C.; Li, L. X.; Zheng, J. X.; Ren, Y.; Wu, T. P.; Shahbazian-Yassar, R.; Wen, J. G.; Pan, F.; Amin, K. Correlation between manganese dissolution and dynamic phase stability in spinel-based lithium-ion battery. *Nat. Commun.* **2019**, 10, 4721.
- (5) Zhang, H. L.; May, B. M.; Serrano-Sevillano, J.; Casas-Cabanas, M.; Cabana, J.; Wang, C. M.; Zhou, G. W. Facet-dependent rock-salt reconstruction on the surface of layered oxide cathodes. *Chem. Mater.* **2018**, 30, 692–669.
- (6) Zou, L. F.; Liu, Z. Y.; Zhao, W. G.; Jia, H. P.; Zheng, J. M.; Yang, Y.; Wang, G. F.; Zhang, J. G.; Wang, C. M. Solid-liquid interfacial reaction triggered propagation of phase transition from surface into bulk lattice of Ni-rich layered cathode. *Chem. Mater.* **2018**, 30, 7016–7026.
- (7) Yan, P. F.; Zheng, J. M.; Liu, J.; Wang, B. Q.; Cheng, X. P.; Zhang, Y. F.; Sun, X. L.; Wang, C. M.; Zhang, J. G. Tailoring grain boundary structures and chemistry of Ni-rich layered cathodes for enhanced cycle stability of lithium-ion batteries. *Nat. Energy* **2018**, 3, 600–605.
- (8) Xu, G. L.; Liu, Q.; Lau, K. K. S.; Liu, Y.; Liu, X.; Gao, H.; Zhou, X. W.; Zhuang, M. H.; Ren, Y.; Li, J. D.; Shao, M. H.; Ouyang, M. G.; Pan, F.; Chen, Z. H.; Amine, K.; Chen, G. H. Building ultraconformal protective layers on both secondary and primary particles of layered lithium transition metal oxide cathodes. *Nat. Energy* **2019**, 4, 484–494.
- (9) Ryu, J.; Chen, T. W.; Bok, T.; Song, G.; Ma, J.; Hwang, C.; Luo, L. L.; Song, H. K.; Cho, J.; Wang, C. M.; Zhang, S. L.; Park, S. Mechanical mismatch-driven rippling in carbon-coated silicon sheets for stress-resilient battery anodes. *Nat. Commun.* **2018**, 9, 2924.
- (10) Li, L. Z.; Yu, J. G.; Darbar, D.; Self, E. C.; Wang, D. H.; Nanda, J.; Bhattacharya, I.; Wang, C. M. Atomic-scale mechanisms of enhanced electrochemical properties of Mo-doped Co-free layered oxide cathodes for lithium-ion batteries. *ACS Energy Lett.* **2019**, 4, 2540–2546.
- (11) Zou, L. F.; Li, J. Y.; Liu, Z. Y.; Wang, G. F.; Manthiram, A.; Wang, C. M. Lattice doping regulated interfacial reactions in cathode for enhanced cycling stability. *Nat. Commun.* **2019**, 10, 3447.
- (12) Ryu, J.; Seo, J. H.; Song, G.; Choi, K.; Hong, D.; Wang, C.; Lee, H.; Lee, J. H.; Park, S. Infinitesimal sulfur fusion yields quasi-metallic bulk silicon for stable and fast energy storage. *Nat. Commun.* **2019**, 10, 2351.
- (13) Cao, X.; Ren, X. D.; Zou, L. F.; Engelhard, M. H.; Huang, W.; Wang, H. S.; Matthews, B. E.; Lee, H.; Niu, C. J.; Arey, B. W.; Cui, Y.; Wang, C. M.; Xiao, J.; Liu, J.; Xu, W.; Zhang, J. G. Monolithic solid-electrolyte interphases formed in fluorinated orthoformated-based electrolytes minimize Li depletion and pulverization. *Nat. Energy* **2019**, 4, 796–805.
- (14) Ren, X. D.; Zou, L. F.; Jiao, S. H.; Mei, D. H.; Engelhard, M. H.; Li, Q. Y.; Lee, H. Y.; Niu, C. J.; Adams, B. D.; Wang, C. M.; Liu, J.; Zhang, J. G.; Xu, W. High-concentration ether electrolytes for stable high-voltage lithium metal batteries. *ACS Energy Lett.* **2019**, 4, 896–902.
- (15) Zhao, W. G.; Zou, L. F.; Zheng, J. M.; Jia, H. P.; Song, J. H.; Engelhard, M. H.; Wang, C. M.; Xu, W.; Yang, Y.; Zhang, J. G. Simultaneous stabilization of $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}\text{O}_2$ cathode and lithium metal anode by lithium bis(oxalato)borate as additive. *ChemSusChem.* **2018**, 11, 2211–2220.
- (16) Zou, L. F.; Zhao, W. G.; Liu, Z. Y.; Jia, H. P.; Zheng, J. M.; Wang, G. F.; Yang, Y.; Zhang, J. G.; Wang, C. M. Revealing cycling rate-dependent structure evolution in Ni-rich layered cathode materials. *ACS Energy Lett.* **2018**, 3, 2433–2440.
- (17) Yan, P. F.; Zheng, J. M.; Chen, T. W.; Luo, L. L.; Jiang, Y. Y.; Wang, K.; Sui, M. L.; Zhang, J. G.; Zhang, S. L.; Wang, C. M. Coupling of electrochemically triggered thermal and mechanical effects to aggravate failure in a layered cathode. *Nat. Commun.* **2018**, 9, 2437.
- (18) Kong, D. F.; Zhang, M. J.; Xiao, Y. G.; Hu, J. T.; Zhao, W. G.; Han, L.; Pan, F. Insights into the structural evolution and Li/O loss in high-Ni layered oxide cathodes. *Nano Energy* **2019**, 59, 327–335.
- (19) Yuan, Y. F.; Amine, K.; Lu, J.; Shahbazian-Yassar, R. Understanding materials challenges for rechargeable ion batteries with *in situ* transmission electron microscopy. *Nat. Commun.* **2017**, 8, 15806.
- (20) Gong, Y.; Zhang, J. N.; Jiang, L. W.; Shi, J. A.; Zhang, Q. H.; Yang, Z. Z.; Zou, D. L.; Wang, J. Y.; Yu, X. Q.; Xiao, R. J.; Hu, Y. S.; Gu, L.; Li, H.; Chen, L. Q. *In situ* atomic-scale observation of electrochemical delithiation induced structure evolution of LiCoO_2 cathode in a working all-solid-state battery. *J. Am. Chem. Soc.* **2017**, 139, 4274–4277.
- (21) Gemmi, M.; Mugnaioli, E.; Gorelik, T. E.; Kolb, U.; Palatinus, L.; Boullay, P.; Hovmöller, S.; Abrahams, J. P. 3D electron diffraction: the nanocrystallography revolution. *ACS Cent. Sci.* **2019**, 5, 1315–13