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Understanding Structure Changes during Cycling of MoS_2-based Mg Batteries

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Aberration-corrected (scanning) transmission electron microscopy ((S)TEM) has been used as an important tool to characterize battery materials. However, the dis/charge processes often generate a large number of defects in the electrode materials strongly distorting their crystalline structure or even making them amorphous. At the same time, the solid electrolyte interface (SEI) is formed and they are electrolyte coated after cycling. This intrinsically limits application of atomically resolved imaging techniques and even conventional diffraction. Furthermore, the signal of analytical methods such as EDX and EELS spectral imaging is obscured as the nanosized electrode particles are mostly surrounded by carbonaceous additives, which are used for enhancing electron conductivity of the battery electrode in the realistic electrochemical environment[1].

The atomic pair distribution function (PDF) obtained from diffraction[2], measuring the interatomic distances and coordination, directly probes the atomic configuration, also for strongly distorted or disordered materials. In contrast to X-ray and neutron diffraction, electron diffraction in TEM provides highly flexible spatial resolution from micro- to tens of nanometer[3]. The recently developed 4D STEM-PDF[4] analysis offers PDF mapping with sub-nanometer spatial resolution and, at the same time, samples a statistically meaningful area representing the global sample properties. The power to answer structural questions of complex materials has been demonstrated, e.g. analyzing the structure evolution of phase transformation[3, 5] and the structure of metallic nanoglasses[6].

In this talk, we demonstrate that PDF analysis of electron diffraction in TEM associated with multivariate statistical analysis (MSA) can overcome the above mentioned issues and provide detailed structural and bonding analysis for long-time cycled real batteries. We explore our approach using MoS_2-based Mg batteries, as the rechargeable Mg batteries are one of the most promising candidates for the next generation battery technologies. However, the crystalline structure of the host material is significantly destroyed during cycling because of the strong interaction between double charged Mg^{2+} and the intercalation host, which leads to a transition from a short- and medium range order similar to 1H MoS_2 to 2T MoS_2 during cycling. As shown in figure 1, we detected the intercalation of solvated magnesium-ions ([Mg(DME)x]2+) in the layered MoS_2 cathode[7]. This proves that the high charge density of Mg^{2+} may be mitigated through dimethoxyethane solvation, which avoids the sluggish desolvation process at the cathode electrolyte interfaces and reduces the trapping force of the cathode lattice to the cations, facilitating Mg^{2+}diffusion. In addition, the 4DSTEM-PDF line scan in the charged sample (figure 1f and g) reveals a thin surface layer containing reduced Mo and atomic arrangement differing from the H-type bulk. It explains the ambiguous correlation between the X-ray photo-emission spectroscopy (XPS) result and the electrochemistry[8].

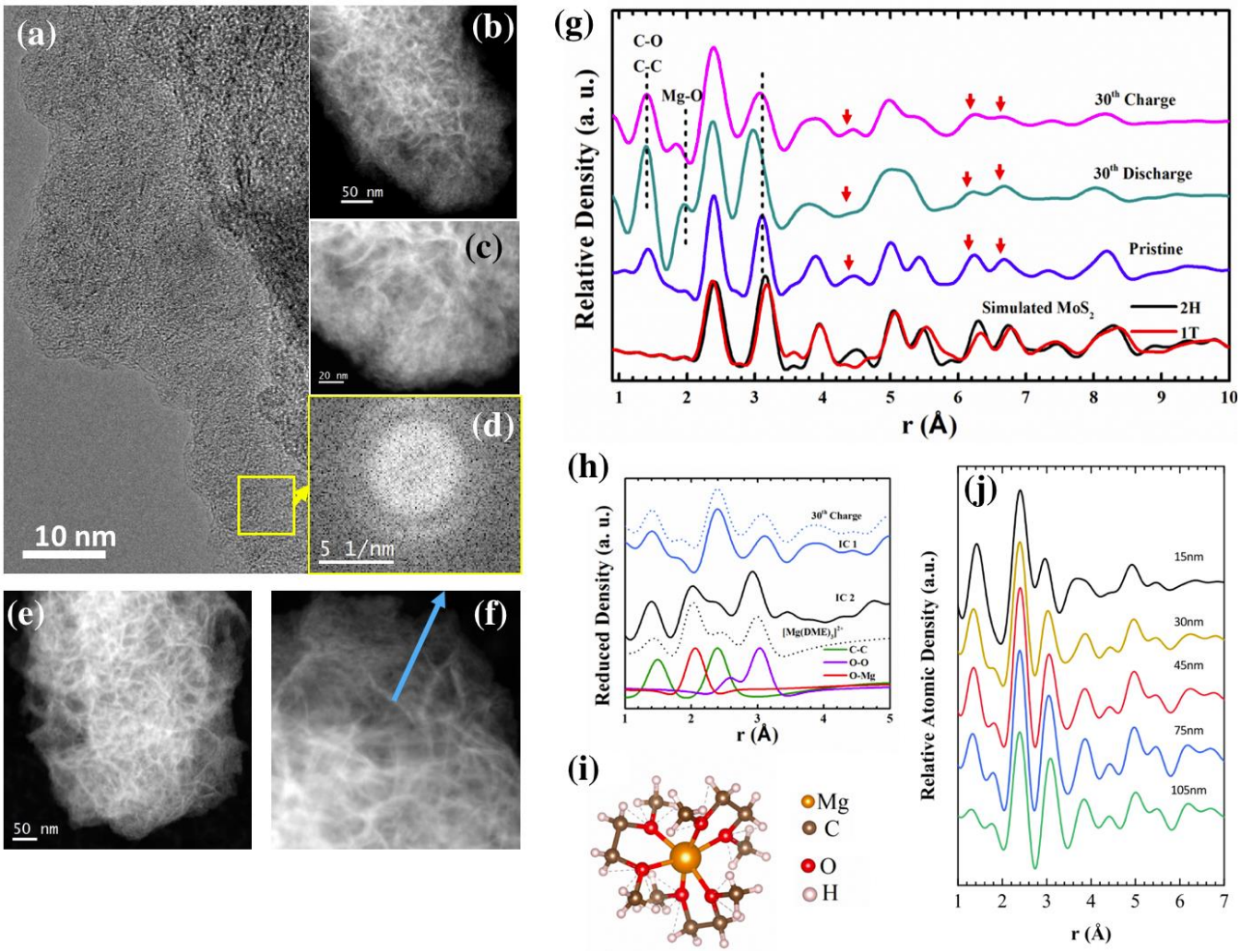

Fig. 1 HRTEM image (a) and STEM-HAADF image (b, c) of 30th cycled MoS_2 at discharged (Mo^{2+}-in) state, (d) the FFT from the area highlighted in (a). (e) and (f) are STEM-HAADF images of the 30th charged (Mo^{2+}-out) state. (g) PDF analysis of diffraction patterns taken from a 100×200 nm area, and the simulated PDFs of 2H-MoS_2 (dotted green curve) and distorted 1T-MoS_2 (dotted black curve). (h) MSA solution to the PDF curves, and the simulated PDF of a $[Mg(DME)_3]^{2+}$ molecular cluster. (i) Molecular structure of a $[Mg(DME)_3]^{2+}$ cluster. (j) local PDFs at different depth from the surface of the 30th charged sample, taken along the line highlighted in (f).

[1] C Zhu et al., Science **358**, 1400 (2017).
[2] T. Egami et al., Underneath Bragg Peaks Struct. Anal. Complex Mater. **16**, 55 (2012).
[3] X. Mu et al, J. Appl. Crystallogr. **46**, 1105 (2013).
[4] X. Mu et al, Ultramicroscopy **168**, 1, (2016).
[5] X. Mu et al, Z. Anorg. Allg. Chem. **640**, 1868–1875, (2014)
[6] Y. Ivanisenko et al, Adv. Eng. Mat. **1**, 1800404, (2018).
[7] Z. Li et al, Nat. Commun. **9**, 5115 (2018).
[8] X. Mu acknowledge Deutsche Forschungsgemeinschaft's (MU 4276/1-1) support for the development of STEM-PDF.

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