Reaction and Nucleation Pathways in a Conversion Reaction Lithium-Ion Battery Anode

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Abstract

Transition metal oxides have received broad interests as anode materials for Li-ion batteries on account of their high specific capacity and volumetric energy density compared with traditional graphitic anodes. During lithiation, a class of transition metal oxides, such as NiO, undergo conversion reaction where Li ions and transition metal oxides are converted to Li-O compounds and transition metal nanoparticles respectively.[1] Although electrochemistry of conversion reaction anodes has been well studied, the spatial-dependent lithiation pathways during lithiation and de-lithiation still remain elusive. In addition to the lithiation/de-lithiation process, solid-electrolyte interface (SEI) forms during electrochemical cycling. SEI serves as a passivation layer for electrode materials, and it is one of the significant contributors to irreversible capacity. The chemical and physical properties of SEI layers can significantly modify electrochemical performance of transition metal oxide anodes, such as rate capability; therefore, it is critically important to uncover the structure and composition of SEI layer.

Herein, we tackle these challenges using highly oriented NiO nanosheets[2] as active anode materials. The experimental design is illustrated in Figure 1a, where a TEM grid loaded with NiO nanosheets was placed in between separator and normal battery electrode (i.e., NiO active materials, additive carbon, binder). The TEM grid was carefully removed, rinsed with dimethyl carbonate and dried overnight in a He-filled glove box after designated electrochemical cycles (exemplified in Figure 1c). A representative TEM image of a NiO nanosheet with 50% state of charge is shown in Figure 1b, which clearly demonstrates a heterogeneous nucleation phenomenon during lithiation. Furthermore, HAADF-STEM imaging and 3D tomographic reconstruction reveal that lithiation results in a nanoporous Ni network imbedded in a Li-C-O matrix instead of widely reported Ni nanoparticles. With the aid of STEM-EELS and electron diffraction, the chemical environment and crystal structure of SEI layer were successfully unraveled. Finally, bulk sensitive synchrotron X-ray absorption spectroscopy and diffraction were performed on normal electrodes to confirm the consistency of nanoscale observation (i.e., STEM-EELS, electron diffraction) to large-scale experimental results.
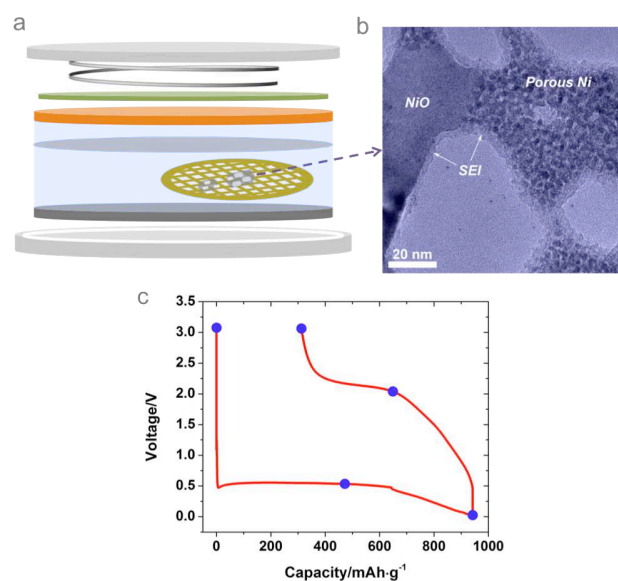
Figure 1. (a) Schematic illustration of the coin cell design with a TEM grid, (b) a representative TEM image for a NiO nanosheet with 50% state of charge, and (c) first galvanostatic cycle (0.5C rate, 359 mA/g) of NiO nanosheets in a 1 M $LiPF_6$ electrolyte dissolved in ethylene carbonate: dimethyl carbonate (1:2)

References

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