Lithium-excess disordered rock-salt oxides have opened up a new vista in search of high-capacity cathodes, resulting in a variety of new materials with versatile elemental compositions. This work introduces W6+ as a possible charge-compensator and explores the solid-solution series Li1+x/100Ni1/2−x/120Ti1/2−x/120Wx/150O2 (x = 0, 5, 10, 15, 20), which have been rationally developed based on concepts from percolation theory. Consistent with this understanding, the specific capacities increase from stoichiometric towards lithium-excessive compositions, while simultaneously capacity retention decreases considerably. Specifically, Li1.2Ni0.333Ti0.333W0.133O2 exhibits a first charge capacity of 246 mAh g⁻¹, which exceeds the theoretical transition metal redox capacity. To understand this peculiarity, we characterize the redox mechanism of Nickel, Titanium, Tungsten, and oxygen using X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, density-functional theory calculations, and differential electrochemical mass spectroscopy. We demonstrate that oxygen evolution takes place for Li1.2Ni0.333Ti0.333W0.133O2 predominantly at 4.4 V vs. Li+/Li, but was absent for the stoichiometric LiNi0.5Ti0.5O2. The oxygen redox causes instability of the anion framework, resulting in oxygen loss from the surface, which incurs severe capacity fading and leads to the observed voltage hysteresis. These finding provide important implications for the development and design of novel high capacity lithium-excess nickel based cathode materials.


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