

Elucidation of Charge Compensation Mechanisms of Li-excess Vanadium Oxides on Li Extraction

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1 Introduction

High-energy and long-life lithium-ion batteries are necessary because of growth of EVs market. Recently, Li-excess materials have been extensively studied as potential high-capacity positive electrode for lithium-ion batteries. In our group, $\text{Li}_3\text{NbO}_4\text{-LiVO}_2$ binary system with vanadium two-electron redox reaction was targeted and reported as high-capacity electrode materials. Among the tested samples, cation-disordered rocksalt-type $\text{Li}_{1.25}\text{Nb}_{0.25}\text{V}_{0.5}\text{O}_2$ (s.g., *Fm-3m*) delivers a larger reversible capacity 250 mA h g^{-1} . [1] In this study, for further improvement of electrochemical properties, carbon-coated samples were synthesized and evaluated to elucidate reaction mechanisms on charge/discharge processes.

2 Experiment

$\text{Li}_{1.25}\text{Nb}_{0.25}\text{V}_{0.5}\text{O}_2$ were prepared by conventional calcination method from a stoichiometric amount of Li_2CO_3 , Nb_2O_5 , and V_2O_3 at 950 °C for 12 h in argon atmosphere. The carbon-coated samples with different particle size were synthesized by annealing after wet or dry ball milling with carbon sources. Electrochemical properties of the oxides were studied by galvanostatic charge/discharge measurement in two-electrode cells. XAS measurement were conducted, and K-edge spectra of vanadium were collected at each charge condition.

3 Results and Discussion

Among the synthesized samples, carbon coated $\text{Li}_{1.25}\text{Nb}_{0.25}\text{V}_{0.5}\text{O}_2$ denoted by “3-Dry&Wet” in Fig. 1 delivers a large reversible capacity of over 250 and 170 mA h g^{-1} at 10 and 2560 mA g^{-1} , respectively. XANES spectra at V K-edge for this sample at each charge state are shown in Figure 2. The energy of V K-edge spectra in this sample shift toward the high energy region on charge, and pre-edge peak at 5468 eV is also intensified, suggesting that vanadium ion oxidation and migration from original octahedral into tetrahedral sites. On discharging, K-edge spectra shift back toward its original position, and the reduction of pre-edge peak intensity is also observed. These finding suggests that vanadium two-electron redox ($\text{V}^{3+}/\text{V}^{5+}$) is highly reversible without the sacrifice electrode kinetics even though V ions migrate between octahedral and tetrahedral sites. From these results, it is concluded that carbon-coated

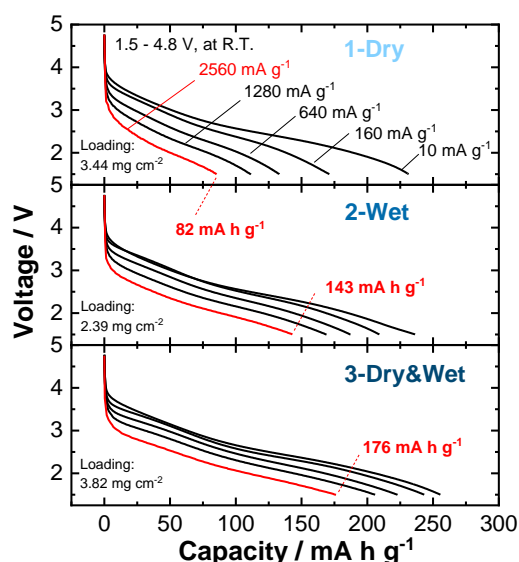


Fig. 1: Galvanostatic charge/discharge curves of carbon-coated $\text{Li}_{1.25}\text{Nb}_{0.25}\text{V}_{0.5}\text{O}_2$ in a Li cells at 10-2560 mA g^{-1} . “Dry” and “Wet” indicate ball milling conditions with or without solvent when mixed with carbon precursors. [2]

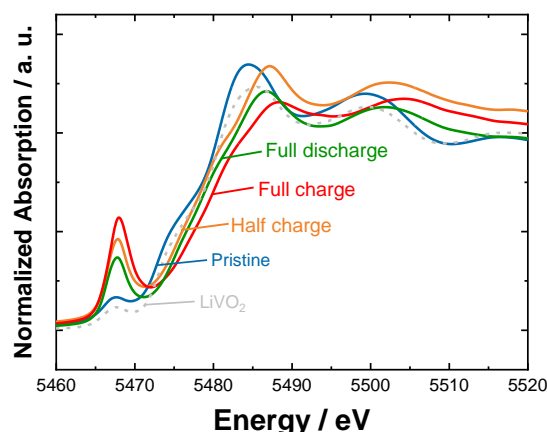


Fig. 2: V K-edge XAS spectra of $\text{Li}_{1.25-y}\text{Nb}_{0.25}\text{V}_{0.5}\text{O}_2$ on the charge/discharge processes. The data of LiVO_2 used as a reference material is also shown for comparison.

Li-excess V/Nb oxides are used as potential high-capacity electrode with good rate capability based on reversible $\text{V}^{3+}/\text{V}^{5+}$ two-electron redox in the future. [2]

References

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- [2] R. Qi *et. al.*, and N. Yabuuchi, *Chem. Mater.* **34**, 1946 (2022).

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