Development of High-energy-density Spinel Oxide Cathode Materials for Lithium-ion Batteries

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Introduction

Lithium-ion batteries (LIBs) have been widely used in various applications such as mobile devices, power leveling of renewable energies and electronic vehicles, and for the above-mentioned applications, increasing energy density of cathode materials is essentially important. For that purpose, achieving high-capacity charge/discharge reactions at a high voltage region are necessary [1]. In LIBs, a lower lithium activity leads to a higher operating voltage, however, achieving high capacity requires a higher lithium content. To improve the energy density by rational tuning of defect structures, in this study, we modify cation/anion defects in a spinel-type $LiNi_{0.5}Mn_{1.5}O_4$ and investigate their electrochemical properties.

Experimental Procedures

The pristine material, $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO), was synthesized by the solid-state method. $Li_{1.1}Ni_{0.55}Mn_{1.35}O_{3.2}F_{0.4}$ (LNMOF-0.1) was synthesized by ball milling of stoichiometric precursor mixtures and post-annealing. Crystal structures of all samples were characterized by X-ray diffraction. The cathode materials were made of 70 wt% samples, 20 wt% conductive carbon black, and 10 wt% PVDF with NMP used as the solvent. A coin cell was assembled from the synthesized cathode, liquid organic electrolyte (1 M $LiPF_6$ in EC: DMC (3:7) solution), and lithium metal as counter electrode. Electrochemical measurements were carried out by 0.1 rate charge/discharge cycling in the voltage range of 3.5 V～5.0 V.

Results and Discussion

Figure 1 exhibits the XRD patterns of LNMO and LNMOF-0.1 samples. The diffraction peaks of all samples were consistent with the patterns of the spinel oxide. In LNMOF-0.1, the peak intensity of (220) increased compared to LNMO, suggesting the site mixing of lithium ions and nickel ions [2]. Since the ionic radii Li^+ and Ni^{2+} are 0.76 Å and 0.69 Å, it is reasonable that such cation mixing proceeded as observed in earlier works on $LiNiO_2$ [3]. Figure 2 exhibits Charge-discharge profiles of the second cycle of LNMO and LNMOF-0.1. Both samples showed two voltage plateaus at 4.7 V and 4.75 V ascribed to the Ni^{4+}/Ni^{2+} redox, and very short plateau around 4.0 V ascribed to slight Mn redox [4]. In LNMOF-0.1, charge/discharge capacity at a high voltage range ascribed to the nickel redox was observed. However, discharge capacity decreased compared to LNMO. This is probably because smooth Li migration was hindered by immobile Ni defects in Li migration path. In the presentation, we will also report on structure analysis and electrochemical properties.

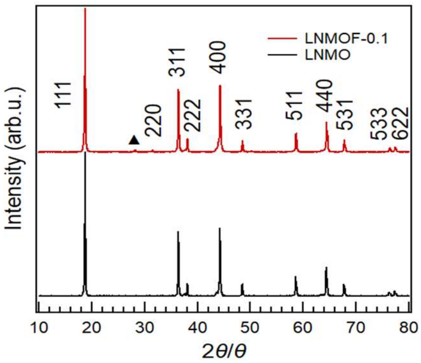

Fig. 1 XRD patterns of LNMO and LNMOF-0.1

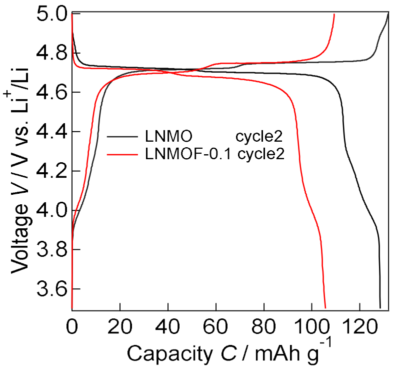

Fig. 2 Charge-discharge profiles

References

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