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Electrochemistry and redox characterization of rock-salt-type lithium metal oxides $Li_{1+z/3}Ni_{1/2-z/2}Ti_{1/2+z/6}O_2$ for Li-ion batteries

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This work explores the compound $Li_{1+z/3}Ni_{1/2-z/2}Ti_{1/2+z/6}O_2$ (z = 0, 0.1, 0.2, 0.3, 0.4, 0.5) and compares the electrochemical performance difference with z to the proposed percolation network. X-ray diffraction combined with Rietveld refinements show that rock-salt structure is obtained by the simple sol-gel process, and the lattice parameters are increased with the increasing level of Li-excess. Micromorphology observation reveals that particles are irregular and the size is distributed within 100 nm. In addition, a detailed reaction mechanism is examined by X-ray photoelectron spectroscopy and cyclic voltammetry, which exhibits the evolution of Ni, Ti and O in the initial charge-discharge process and confirms that they all make contributions to capacities. Electrochemical performance test shows that the discharge capacities increase with the amount of Li and $Li_{1.17}Ni_{0.25}Ti_{0.58}O_2$ delivers the discharge capacities up to 223.9 mAh g^{-1}. At the current density of 400 mA g^{-1}, it still provides a large capacity of 120 mAh g^{-1}. Furthermore, $Li_{1.17}Ni_{0.25}Ti_{0.58}O_2$ has the highest lithium ion diffusion coefficient among all samples.

1. Introduction

Li-ion batteries are the dominant contender among rechargeable batteries because of their high energy densities. In order to achieve the goal of widespread use of Li-ion batteries, researchers from the entire world have investigated a wide range of electrode materials [1–6]. In particular, the layered $LiMO_2$ (M = transition metal), spinel $LiMn_2O_4$ and olivine and these structures so far have been immensely investigated owing to their excellent properties.

Among the positive electrode materials reported so far, Li-excess materials, $Li_{(1+x)}M_{y(1-x)}N_{(1-y)(1-x)}O_2$ layered materials with rock-salt-type structures, have been intensively studied for high capacity batteries, which can deliver up to more than 200 mAg h^{-1}. Nevertheless this type of cathode materials suffers from irreversible capacity fading and voltage decay because of cations mixing in the rock-salt lattice and oxygen release in the charging process [7–10]. However, recent progress in cation-disordered materials $Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ [11] has confirmed that disordered Li-excess materials can also show enhanced performance between 1.5 and 4.3 V. This is because increasing Li content to exceed ~1.09 can form 0-TM channels to a percolating network, which can provide more fast migration channels for lithium ions. This strategy could ensure that Li-excess materials can obtain high capacity and density without the effect of cation mixing. Currently, many disordered rock-salt-type oxides, sulphides and ox fluorides have been developed [12–19] and oxides as electrode materials commonly show better electrochemical performance.

To utilize the Li-excess rock-salts as the electrode materials, extensive efforts have been made to study the mechanism of redox activity over the past years. The redox process of some 3D and 4D transitional metals have been examined in different compounds, including the system of Li-M-Ti-O (M = Fe, Mn, Ni, V, Ru), Li_3MO_4 (M = Nb, Mo). In the disordered oxides, Li-M-Ti-O, it is generally believed that transitional metals show different properties in the charging process. In-situ ^{57}Fe Mössbauer and XPS have ever been taken to study the redox process of Fe and Tabuchi et al. found that

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Fe^{3+}/Fe^{4+} redox could be only detected at around 4 V [20–22]. However, for the V-doping sample, Fe is not oxidized to tetravalent state [23]. In-situ XANES spectra have shown that Mn can be oxidized to +3 below 4.3 V and they cannot be oxidized to higher valence because of the anion redox and side reactions in $Li_{2.4}Mn_{0.8}Ti_{0.8}O_4$ [24]. XANES and XPS are also used to characterize the valence state of V and Ru and confirm that they can be oxidized to +3.8 and + 5 in titanates oxides, respectively [25,26]. To our knowledge, however, little work has been done on Li-excess rock-salts Li-Ni-Ti-O. Current work is limited to the studies on Li_2NiTiO_4, $LiNi_{0.5}Ti_{0.5}O_2$ and $LiNi_yTi_{1-y}O_2$ and the valence state of Ni is still unclear during cycling [27–31]. In addition, Ti is often considered to be electrochemically inactive and there is a discrepancy about whether there is reduction of Ti^{4+} in titanates oxides [12,21,26,27]. However, 4D transmission metals Nb and Mo almost remain at the original valence in different disordered rock-salts, and they play the role of stabilizing the crystal structure [12,15,32,33]. Apart from the contributions from cations, the anionic redox processes are also regarded as a contributor to capacities, but oxygen loss can also cause some side effects simultaneously during cycles, which may cause structure shrink and irreversible loss [8,12,14,34–36].

In this study, the oxide cathodes Li-Ni-Ti-O were synthesized through a sol-gel route and the redox mechanism of this compound was investigated. A broader voltage region (1.5–4.5 V) was used to examine the cationic (Ni^{2+}, Ti^{4+}) and anionic (O^{2-}) redox couple reaction. In addition, the effects of content of Li on the structure, morphology and electrochemical performance were investigated. The relationships between the valence changes and structure evolution were also analyzed. Furthermore, the kinetics of Li diffusion were also studied to describe Li mobility and quantify the number of 0-TM channels.

2. Experimental

2.1. Synthesis

Sol-gel method was used to synthesize the $Li_{1+z/3}Ni_{1/2-z/2}Ti_{1/2+z/6}O_2$ nanoparticles in our previous work [37]. Stoichiometric amounts of lithium acetate dehydrate and nickel acetate dehydrate were firstly dissolved into ethanol and then appropriate amount of ethylene glycol was added as dispersing agent. Then stoichiometric tetra-butyl titanate was added into the mixed solution. Then the mixture was heated and maintained at 80 °C for 24 h by oil bathing. After ethanol was evaporated, the sol was dried in oven at 100 °C. Then the xero-gel was processed by ball milling for 5 h at 300 r/min. Finally, the powders were sintered at 600 °C for 10 h in air. $Li_{1+z/3}Ni_{1/2-z/2}Ti_{1/2+z/6}O_2$ samples with Z = 0, 0.1, 0.2, 0.3, 0.4, 0.5 are referred to LNTO, LNTO1, LNTO2, LNTO3, LNTO4 and LNTO5, respectively.

2.2. Electrochemistry

2025 cells were prepared according to the standard procedures. Firstly, cathode film was prepared using the LNTO powder, acetylene black and poly binder at the ratio of 8:1:1, and then coated onto a Al foil. Secondly, the half-cell was assembled inside an argon-filled glove box, 1 M $LiPF_6$ EC/DMC solution (EC:DMC = 1:1), lithium metal and Celgard 2500 polypropylene were used as electrolyte, the negative electrode and the separator, respectively. Finally, cells were examined at room temperature with a voltage range between 1.5 and 4.5 V with a constant current density of 40 mA g^{-1}.

2.3. Characterization

The X-ray diffraction (XRD) patterns were collected on a Rigaku multipurpose diffractometer using Cu Kα radiation in the two-theta range of 10–85°. Scanning electron microscopy (SEM) images were collected on a JEOL JSM-7800F SEM. Transmission electron microscopy (TEM) analysis was performed with a Hitachi-7650 operated at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) of the compounds was detected on the Thermo ESCALAB 250XI. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) have been carried out with a CHI 660E electrochemical workstation.

3. Results and discussion

3.1. Structural and morphological characterization

Fig. 1a exhibits the XRD patterns of $Li_{1+z/3}Ni_{1/2-z/2}Ti_{1/2+z/6}O_2$ and the crystal structure of the as-prepared sample is determined by Rietveld structural refinement. The diffraction patterns can be well indexed to the cubic rock salt structure (Fm-3m space group). Crystallographic information file of Fm-3m $LiFeO_2$ (ICSD 51208) is used as an input file. The refined cell parameters and the agreement factors are listed in Table 1. It can be seen from Table 1 that the lattice parameter a, increases with the level of Li-excess. This is because the average cationic radius of Li_2TiO_3 is bigger than that of $LiNi_{0.5}Ti_{0.5}O_2$ (0.707 vs. 0.702 Å). As illustrated in Fig. 1b, Li, Ni and Ti atoms distribute randomly at 4a sites and the O occupancy is at 4b site. For example, the refined occupancy ratio of Li/Ni/Ti is 0.58/0.14/0.26 and the ratio of O is 1 in the LNTO5. Averagely, this is coordinated with the cationic and anionic atoms in the stoichiometric $Li_{1.17}Ni_{0.25}Ti_{0.58}O_2$.

Fig. 2 displays scanning electron microscopy, high resolution transmission electron microscopy images and energy dispersive spectroscopy mapping of the LNTO5. The LNTO5 has the best electrochemical properties among all the samples. Fig. 3a–f shows the morphologies of $Li_{1+z/3}Ni_{1/2-z/2}Ti_{1/2+z/6}O_2$ and it is obvious that the particles are well-distributed and the average size is around 100 nm, which is consistent with the size of Li_2NiTiO_4 synthesized by citrate-precursor method and Li_2NiTiO_4 shows better performance at particle size of 100 nm [38]. However, with the increasing level of Li-excess, the LNTO5 shows more agglomeration and this may be assigned to high content of Ti, whose starting material tetra-butyl titanate is easy to hydrolyze. It is relatively hard to control the time of hydroxylation when the amount of tetra-butyl titanate increases, which result in more severe agglomeration. TEM images confirm the size of these particles and show more detailed structure of LNTO, LNTO3 and LNTO5, as shown in Fig. 2g–i. Clear lattice fringes in the HRTEM image of Fig. 2j confirm good crystallinity of LNTO5 particles and the lattice space of 0.129 nm corresponds to the (200) plane of LNTO5. The SAED pattern show cation-disordering reflections and all planes marked in diffraction rings confirm the polycrystalline cubic structure of LNTO5. The distribution of cation and anion are characterized by EDS mapping, as shown in Fig. 2l–o. Nickel, titanium and oxygen ions are distributed uniformly.

3.2. Redox mechanism analysis

The rock-salt-type LNTO, LNTO1, LNTO2, LNTO3, LNTO4, and LNTO5 were employed as electrode active materials for lithium ion batteries respectively. Fig. 3a shows the initial charge-discharge curves of these six samples at the current density of 20 mA g^{-1} between 1.5 and 4.5 V. It is noticeable that the charge-discharge capacities increase with the increasing amount of Li, as shown in