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ORIGINAL PAPER

Electrochemical lithium and sodium insertion studies in 3D metal oxy-phosphate framework $MoWO_3(PO_4)_2$ for battery applications

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Abstract
A new type of three-dimensional (3D) oxy-phosphate materials are explored for the application of Li and Na batteries. The molybdenum tungsten oxy phosphate, $MoWO_3(PO_4)_2$, was synthesized by solid-state method and evaluated for Li/Na insertion/de-insertion electrode material for the first time. The cell at charged state (vs. Li^+/Li) showed a discharge capacity of 786 mAh g^{-1} within the voltage window of 0.3 V with amorphization of crystalline $MoWO_3(PO_4)_2$ as observed from ex-situ powder XRD analysis. The structural integrity was revealed in this material, even with nearly more than 5 Li^+ ions into the lattice, leading to the discharge capacity of 250 mAh g^{-1}. The reversible charge/discharge behavior with insertion/de-insertion of 2.4 Li^+ ions in the voltage range of 1.65 – 3.5 V resulted in 110 and 95 mAh g^{-1} at C/10 and C/5 rates, respectively. On the other hand, poor cycling performance was noticed for Na ion insertion and desertion, with a discharge capacity of 250 mAh/g within the voltage range of 0.3 – 3.5 V (vs. Na^+/Na).

Keywords $MoWO_3(PO_4)_2$ · X-ray diffraction · Li and Na insertion · Electrochemical properties

Introduction

Lithium insertion and de-insertion in tungsten and molybdenum-based oxides have been extensively studied for Li and Na-ion batteries. The reported phases of molybdenum/tungsten oxides and alkali molybdenum/tungsten oxides include MoO_3, WO_3, A_xMoO_3 (A = Li, Na), Li_2MoO_3, and $Li_5Mo_5O_{12}$ [1–4]. These oxides showed Li-ion insertion and de-insertion of 2 to 3 Li ions into and from the structure, respectively, in the voltage range of 0.5 – 4.3 V [4–6]. Recently, the triclinic $Li_4Mo_5O_{17}$ phase (space group, $P-1$) reported by Pop et al. has edge shared MoO_6 polyhedra, resulting in a ribbon type structure. The insertion of 7 Li-ions into the triclinic $Li_4Mo_5O_{17}$ phase result in a rock salt type $Li_{11}Mo_5O_{12}$ phase. De-insertion of 7 Li-ions shows the formation of the parent phase, cycled at a C/100 rate in the voltage window of 2.2 – 3.0 V [7]. The garnet framework compound, $Li_3Nd_2W_2O_{12}$, has been explored for Li-ion batteries and shows the possibility of reversible insertion and de-insertion of Li ions.

New polyanionic materials, especially phosphate-based compounds, are considered structurally and thermally resistant during charge/discharge cycling with fast diffusion of Li and Na ions [8, 9]. For instance, $LiFePO_4$ with olivine structures is the best example of the cathode material of choice for Li-ion battery applications in plug-in hybrid electric vehicles. This is because of its structural integrity and thermal and interface stability during fast diffusion of Li ions at high rate capability [9–11]. NASICON-type materials like $A_3Fe_2(PO_4)_3$ (A = Li or Na), $V_2(SO_4)_3$ [12, 13], and the oxy polyanionic framework compounds such as Li_xMOXO_4 (M = V and Ti; X = S, P and Si) and both α and β forms of $NbO(PO_4)$ have been widely explored as cathode materials recently for Li and Na-ion batteries [14–17]. Due to the availability of easily accessible sites for the intercalated ions to occupy and the presence of metal atoms that

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