Pyrophosphates AMoP$_2$O$_7$ (A = Li and Na): Synthesis, structure and electrochemical properties

Rodion V. Panin[a], Oleg A. Drozhzhin[a,b], Stanislav S. Fedotov[a], Ekaterina A. Suchkova[a], Nellie R. Khasanova[a,*], Evgeny V. Antipov[a]

[a] *Department of Chemistry, Moscow State University, 119991 Moscow, Russia*
[b] *Skolkovo Institute of Science and Technology, 143026 Moscow, Russia*

ARTICLE INFO

ABSTRACT

The carbon-coated single-phase samples of the pyrophosphates AMoP$_2$O$_7$ (A = Li and Na) were synthesized using freeze-drying followed by annealing in a sealed silica tube with the Fe/FeO getter. The Rietveld refinement of the X-Ray powder diffraction data proved both structures are built up as a network of corner-linked MoO$_6$ octahedra and P$_2$O$_7$ groups with A-cations located in the open tunnels running along the [100] (LiMoP$_2$O$_7$) and [101] (NaMoP$_2$O$_7$) directions. The bond valence energy landscapes (BVEL) analysis revealed three-dimensional pathways of alkali-ion migration with significantly different activation energies (0.8 eV for LiMoP$_2$O$_7$ and 4.5 eV for NaMoP$_2$O$_7$) anticipating LiMoP$_2$O$_7$ to exhibit faster Li$^+$ diffusion and better electrochemical characteristics. Both materials displayed electrochemical activity in Li- and Na-cells with reversible capacities of ~20 mA h g^{-1} for NaMoP$_2$O$_7$ and more than 70 mA h g^{-1} for LiMoP$_2$O$_7$, being in a good agreement with the BVEL results.

1. Introduction

Strong research efforts are currently focused on developing rechargeable battery materials with high energy density, low cost and high safety. Polyanion-type materials based on phosphates, silicates, fluoride-sulfates and fluoride-phosphates have received much attention as alternative cathodes for Li- and Na-ion batteries due to their high thermal stability and the inductive effect of polyanion-groups increasing the operating potential of the transition metal redox couple [1,2]. One of the ways towards the enhancement of cathode characteristics is to use multi-electron systems by exploring materials that could cycle more than one lithium/sodium per active transition metal. In this sense, molybdenum-containing materials are worthwhile because Mo is known to easily adopt a wide range of oxidation states (from +3 to +6) preserving a stable octahedral environment. According to the ab-initio analysis by Hautier et al. [3], the potentials of the Mo^{+n}/Mo$^{+(n-1)}$ redox couples (n = 4…6) in phosphates would lie within an acceptable voltage range (3.0–4.5 V range vs. Li/Li$^+$) that makes molybdenum phosphates attractive cathode materials for metal-ion batteries. Nevertheless, only few experimental data on electrochemical properties of these materials have been published so far.

Several papers were devoted to the investigation of Li intercalation in the layered molybdenum oxypyrophosphate δ-(MoO$_2$)$_2$P$_2$O$_7$ [4–6]. It

was shown that up to 1.9 Li per formula unit can be reversibly intercalated in the potential range of 2.3–4.0 V vs. Li/Li$^+$, but further Li-insertion provokes amorphization of the material. The second example of the electrochemically active molybdenum phosphate is Li$_3$Mo$_4$P$_5$O$_{24}$, where Li can be reversibly removed and inserted at 3.8 V and 2.2 V (vs. Li/Li$^+$) correspondingly. The electrochemical activity involves the Mo^{6+}/Mo^{5+} and Mo^{5+}/Mo^{4+} couples indicating multi-electron redox processes [7].

Recently AMP$_2$O$_7$ pyrophosphates (where A = Li or Na and M is a 3d-element) have become objects of permanent investigation as promising electrode materials for metal-ion batteries. The LiMP$_2$O$_7$ materials demonstrate either lithium intercalation or deintercalation depending on the nature of transition metal: reversible lithium insertion was reported for M = Cr and Fe, while for LiVP$_2$O$_7$ both insertion and extraction of Li were observed [8–12]. At the same time, poor electrochemical activity towards sodium de/intercalation was detected for NaFeP$_2$O$_7$ [13] and NaVP$_2$O$_7$ [14]. The molybdenum pyrophosphates AMoP$_2$O$_7$ (A = Li and Na) are isostructural to the corresponding vanadium-based compounds [15–17]. Electrochemical activity of these compounds isolated in the single crystal form has been never tested. Though, the theoretical capacity of the AMoP$_2$O$_7$ pyrophosphates, is not high due to the large atomic mass of molybdenum, investigation of their electrochemical properties and comparison with other pyrophosphate materials might reflect the role of alkali metal environment on

the electrochemical behavior of polyanion-type materials.

In this work we synthesized carbon-coated $AMoP_2O_7$ (A = Li and Na) materials, determined their crystal structures by the X-ray powder diffraction (XRPD) patterns, investigated alkali ion migration systems in $AMoP_2O_7$ structures using the bond valence energy landscapes (BVEL) method and tested electrochemical properties of both materials.

2. Experimental

Carbon-coated materials $AMoP_2O_7$ (A = Li and Na) were synthesized via two-step solid state reaction with lithium acetate (Acros organics, > 99%), sodium oxalate (Reachim, > 98%), $NH_4H_2PO_4$ (Labteh, > 98%) and $(NH_4)_6Mo_7O_{24} \times 4H_2O$ (Sigma, > 99%) as initial reagents. Initial mixtures of reagents were homogenized through mechanical ball-milling or freeze-drying technique. The planetary ball-milling machine (Fritsch Pulverisette 7, WC bowl, 180–200 rpm) was used for reagents mixing and intermediate regrinding. For the freeze-drying method, initial reagents were dissolved in deionized water with an A:Mo:P molar ratio of 1.05:1:2 and molybdenum concentration of 0.05 M (pH 3.5 of the solution was maintained by an acetic acid). The solution formed was pulverized into liquid nitrogen and sublimated within 48 h in the «Labconco» freeze-drying machine (the pressure was kept at 0.1–0.3 mbar) to obtain a cryogranulated powder. The mixtures of reagents (from ball-milling or freeze-drying) were preheated under Ar-flow at 380 °C for 15 h to eliminate CO_2, NH_3 and H_2O. The obtained products were ball-milled with 10 wt.% of acetylene black (Carbon Super C), pelletized and annealed for 10 h under Ar-flow or in sealed silica tubes with metallic getters. Acetylene black acted as a reducing agent and provided conductive carbon coating.

The phase composition of the samples was determined by X-ray powder diffraction (XRPD) data measured on Huber Guinier camera G670 (with an Image Plate detector, Cu $K\alpha_1$ radiation, curved Ge(111) monochromator). Pattern fitting, indexing and lattice parameters refinement were performed with the WinXpow program package. The morphology of the synthesized materials was observed by scanning electron microscopy (Carl Zeiss NVision 40-38-50). X-ray powder diffraction data for the structure refinement were collected by Huber Guinier camera G670 and STOE STADI P diffractometer (linear PSD detector, Co $K\alpha_1$ radiation, curved Ge(111) monochromator, transmission mode). The Rietveld refinement was carried out with JANA2006 software [18].

Electrochemical measurements were carried out in two-electrode cells with Li-foil (or Na-foil) as a counter electrode. To prepare working electrodes the carbon-coated materials were sieved (the ø40 µm «Ekross» sieve) and mixed with the carbon black (Timcal Super-C) and polyvinylidene fluoride binder in a 6:1:1 mass ratio. N-methyl pyrrolidone was added to this mixture to form slurry which was cast uniformly on the Al foil by Doctor Blade© technique. The electrodes were dried at 75 °C for 3 h in air, roll-pressed, punched to round discs (ø10 mm) and vacuum-dried at 120 °C for 3 h. Electrochemical cells were assembled in an Ar-filled glovebox (MBraun, Germany). The solutions of 1 M $LiPF_6$ in EC:DMC (1:1 vol.) or 0.6 M $NaPF_6$ in PC:EC (1:1) served as an electrolyte, borosilicate glass fiber was used as a separator. Galvanostatic cycling with potential limitation (GCPL) were carried out on Biologic VMP-3 (EC-Lab) at C/20 rate (1C ~ 97 mAg^{-1}). The electrochemical evaluation of $LiMoP_2O_7$ in Na-cell started from charging the initial material to 4.2 V (vs. Li/Li$^+$) at rate of C/20, after that the charged electrode was recovered, washed thoroughly with PC and reassembled in Na-cell.

The bond valence energy landscapes (BVEL) analysis [19] for $AMoP_2O_7$ (A = Li and Na) was performed using the 3DBVSMAPPER program (ver. 2.0) [20]. The BVEL script implemented in the program generates a spatial distribution of E(A) energy values (0.02 Å space resolution) calculated according the following formula:

$$E(A) = D_0 \left| \sum_X s_{A-X} - V_{id}(A) \right|^g + E_{asym} + E_{rep},$$

where $\sum_X s_{A-X} - V_{id}(A)$ characterizes the deviation of the bond valence sum of the A mobile ion, surrounded by X counter ions, from the ideal valence of A (V_{id}, equal to 1 in case of Li and Na), E_{asym} designates an energy penalty due to the asymmetry of the coordination of the considered ion and E_{rep} represents the (Coulomb) repulsion. The coefficients D_0 and g as well as a suitable E_{asym} expression can be derived from a Morse-type interaction potential [20]. By adjusting the activation energy parameter [E_{act}, i.e. the difference between the cut-off value of E(A) and minimum E(A), E_{min}] the most energetically favorable space in the structure for Li and Na can be graphically identified and visualized. When continuous this space corresponds to the possible migration pathways for these ions. Within the proposed method, there is a consistent tendency: the lower the E_{act}, the better diffusion properties can be anticipated for the material. E_{act} values for many electrode materials were found to be in good correlation with the energy barriers provided by much complicated calculations based on MD or DFT methodology. The crystal structures and BVEL results were plotted using the VESTA visualization system [21].

3. Results

3.1. Synthesis and characterization

To obtain $AMoP_2O_7$ pyrophosphates (with Mo^{3+}) from the molybdate (Mo^{6+}) source the reduction conditions were applied. At a "preheating" step the color changed from yellowish for the initial mixture to blue or green for the "preheated" products indicating some reduction of Mo(VI) to Mo(V). Deeper reduction of Mo with formation of the $AMoP_2O_7$ phases took place at the following heat treatment, which was properly optimized. The final annealing under Ar-flow typically produced multiphase samples: the samples heated at temperatures < 600 °C contained MoO_2 as a main phase, while MoP prevailed in the samples obtained above 750 °C. The formation of pyrophosphates was observed when the annealing temperature varied within the range of 600–750 °C, however thus prepared samples contained large amount (15–20 wt.%) of impurities (MoO_2 and/or MoP), furthermore the syntheses were rather irreproducible. To avoid these problems we performed the preparation in sealed silica tubes with metallic getters (Ni, Mn, Fe) for adjusting the partial oxygen pressure. Annealing in sealed silica tubes without getter or with Ni gave rise to the $AMoOP_2O_7$ phases (with Mo^{5+}) for both A = Li and Na, at temperatures above 750 °C we also found the NASICON-type $NaMo_2(PO_4)_3$ phosphate containing Mo^{4+}. When synthesis was carried out with Mn getter reduction to MoP was observed. Appearance of the $AMoP_2O_7$ was detected with iron getter, though samples still included some impurities of MoO_2 and MoP. Therefore we had recourse to the freeze-drying technique for homogenizing the initial reagent mixture. The obtained cryogranulates after preheating and intermediate regrinding with acetylene black were annealed in sealed silica tubes with the Fe getter. In this case the pyrophosphates have been already formed at 570 °C. After optimization the pure-phase $AMoP_2O_7$ samples black in color were obtained by heating for 10 h at 650 °C (A = Li) and 600 °C (A = Na).

The XRPD patterns for both $AMoP_2O_7$ (A = Li and Na) were successfully indexed in the monoclinic system with the unit cell parameters matching well with previously reported [16,17]. Careful inspection of the $LiMoP_2O_7$ diffraction pattern revealed weak reflections of WC (1.5 wt.%) coming from the ball-milling procedure, while no impurities were observed for the $NaMoP_2O_7$ sample. For the Rietveld analysis the atomic coordinates previously published [16,17] were taken as starting values. The background profile and peak shape were fitted by a polynomial and a pseudo-Voight functions respectively, atomic