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Anomalous temperature-dependent electrical properties of $Na_2MnP_2O_7$

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$Na_2MnP_2O_7$ is a promising sodium-ion battery cathode material. In our work we analyse electrical properties of $Na_2MnP_2O_7$ ceramics by impedance spectroscopy in the broad frequency range from 10 Hz to 10 GHz. Temperature dependencies of conductivity indicated a phase transition taking place in the grains of ceramics at 663 K, which was also evidenced by differential thermal analysis and thermal X-ray diffraction. In addition, close to the room temperature protonic conductivity strongly influences the total conductivity of the ceramics. Both newly observed phenomena may be important for overall sodium battery performance.

1. Introduction

$NaMO_2$ (M = Ni, Mn, Cr, Co, V) oxides, phosphates like olivine-type $NaFePO_4$ and NASICON-type $Na_3M_2(PO_4)_3$, various fluorophosphates and pyrophosphates were proposed as potential candidates for sodium-ion battery cathode [1]. Among the pyrophosphates, $Li_2FeP_2O_7$ [2–4], $Na_2MnP_2O_7$ [4–6], $NaVP_2O_7$ [7], $Na_2PbP_2O_7$ [8] and $Na_2ZnP_2O_7$ [9–11] compounds have been synthesised and investigated. Attempts to improve the properties of material involved various cationic substitutions in the above mentioned double phosphates, synthesising new compounds such as $Na_2Fe_{1-x}Mn_xP_2O_7$ [12,13], $NaCsMnP_2O_7$, $NaCsMn_{0.35}Cu_{0.65}P_2O_7$ [14], Mn-doped $Na_2ZnP_2O_7$ [15]. There were also attempts to improve the battery cathode by adding carbon nanotubes to sodium iron pyrophosphate [16]. However, the simpler material with chemical composition $Na_2MnP_2O_7$ shows pretty good performance as sodium battery cathode – the reported Mn^{3+}/Mn^{2+} redox potential (vs. Na/Na^+) was 3.6 V and the discharge capacity of 80 mA h g^{-1} was reached [5].

P. Barpanda et al. [5] have shown by theoretical calculations, that $Na_2MnP_2O_7$ triclinic polymorph is the most feasible among the known pyrophosphate structures. The structure of successfully synthesised $Na_2MnP_2O_7$ compound has been refined from X-ray diffraction data in several works. It adopts triclinic symmetry with space group $P\bar{1}$ [6,14] or P1 [5]. The structure consists of MnO_6 octahedrons and MnO_5 tetrahedrons sharing oxygen atom and forming a Mn_2O_{10} unit. Mn_2O_{10} blocks are separated by PO_4-PO_4 (i.e. P_2O_7) units by combined corner- and edge-shared oxygen atoms [5,6]. Such a solid framework provides some channels for Na^+-ion migration.

Although the $Na_2MnP_2O_7$ structure and electrochemical properties were studied in detail, all the investigations on this compound were performed only at room temperature. There is also a lack of extensive conductivity studies of this compound. So, in the current work we study high temperature behaviour of $Na_2MnP_2O_7$ powder and ceramics by differential thermal analysis, thermal X-ray diffraction and high temperature ultra-broadband impedance spectroscopy [17].

2. Experimental

$Na_2MnP_2O_7$ was synthesised by solid state reaction from stoichiometric amounts of $Na_2C_2O_4$, $MnC_2O_4 \cdot 2H_2O$, and $NH_4H_2PO_4$. The initial compounds were mixed in ethyl alcohol for 3 h. The mixture was heated for 6 h at 300 °C in silicon carbide crucible in Ar/H_2 atmosphere, milled and pelletized (500 kg/cm^2). Then the pellet was heated up to 620 °C (ramp rate of 10 °C/min), annealed for 6 h in a tubular furnace under steady Ar/H_2 flow and cooled down to room temperature in Ar/H_2 atmosphere. Finally, the pellet was heated at 700 °C for 6 h, cooled down to room temperature (in Ar/H_2 atmosphere) and milled.

Differential thermal analysis and thermogravimetry (SDT Q600) was performed on heating and cooling the powder from room temperature to 620 °C with 10 K/min heating/cooling rate.

Thermal X-ray powder diffraction (XRPD) has been performed at 30 °C, 100 °C, 300 °C, 400 °C and 500 °C in air with Cu Kα radiation on a Panalytical Xpert MPD diffractometer equipped with the X'Celerator detector and an Anton Paar HTK 12 furnace. The diagrams were recorded in 2θ range from 7 to 80° with a step of 0.017° and 100 s per step.

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For the electrical investigations the powder was pressed and ceramic samples were sintered at 650 °C for 2 h in air. Impedance spectroscopy of the sintered $Na_2MnP_2O_7$ ceramics was performed in the frequency range of 10 Hz–10 GHz and in the temperature range of 300–800 K. Pt paste was applied and fired on the surfaces of cylindrical samples. Most of the impedance measurements were performed in ambient air atmosphere, but in order to clarify the influence of humidity to the electrical properties of $Na_2MnP_2O_7$ ceramics the synthetic air containing <3 ppm of water was used and impedance was measured from 1 to 10^6 Hz with a Frequency Response Analyzer (Solartron 1260) combined with Dielectric Interface (Solartron 1296).

3. Results and discussion

The impedances of $Na_2MnP_2O_7$ ceramics measured at different frequencies and at different temperatures are represented in complex plane plots in Fig. 1.

Typically the impedance spectrum of ion conducting ceramics represented in impedance complex plane plot consists of two consequent semicircles. The one at higher frequencies corresponds to ion migration in the grains of ceramics, while the other at low frequencies corresponds to processes in grain boundaries. The maxima of the imaginary part of impedance is found at the relaxation frequencies, $f_R = 1/RC$,

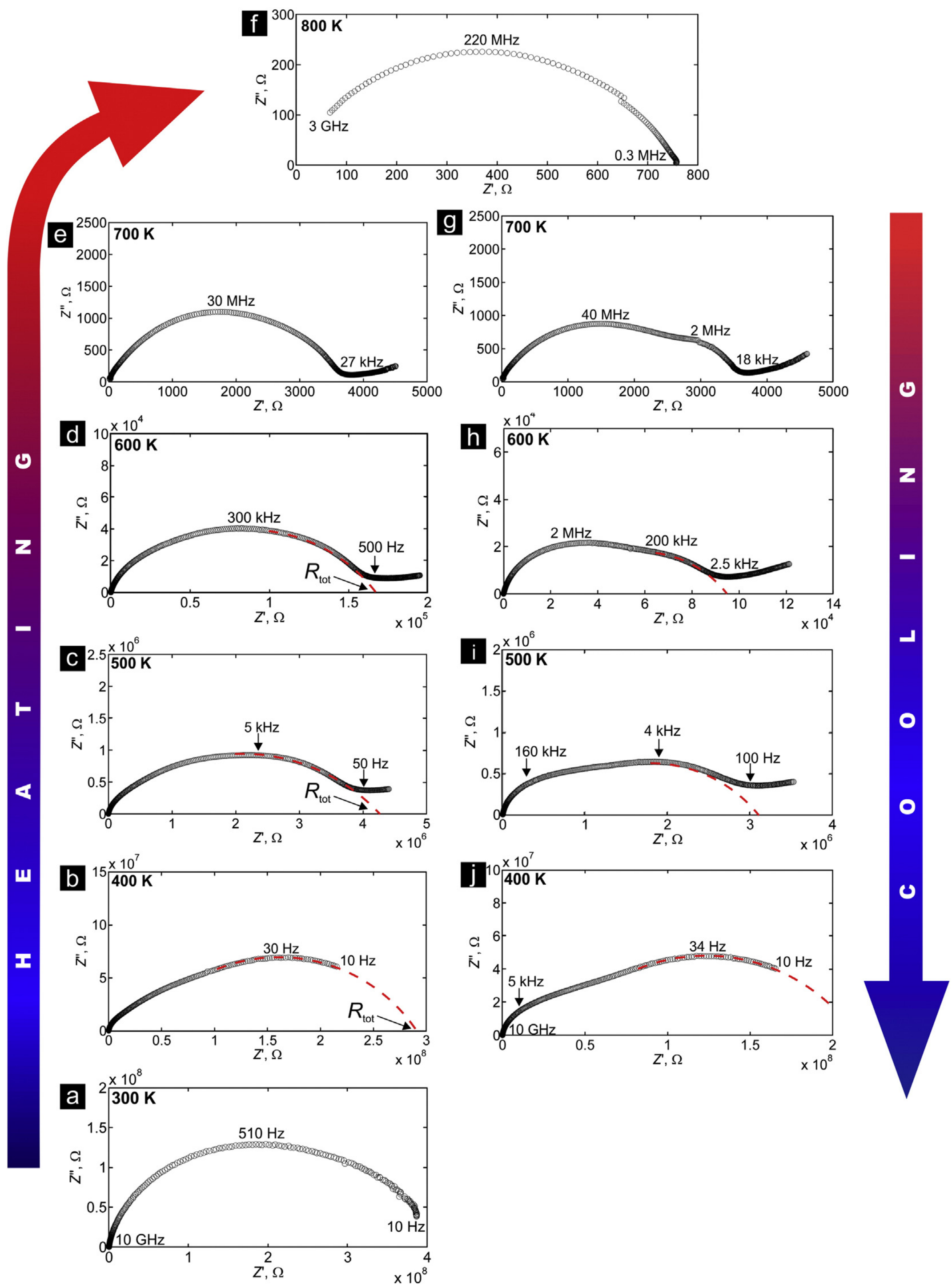

Fig. 1. Impedance complex plane plots of $Na_2MnP_2O_7$ ceramics measured during heating and cooling stages. Some characteristic frequencies are indicated, red dashed lines show extrapolation to total resistance. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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