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Electrical conductivity and charge/discharge profiles of mixed polyanion glass-ceramic cathodes for use in Na-ion batteries

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ABSTRACT

Mixed polyanion glass and glass-ceramic cathodes can have the potential to overcome the disadvantages of achieving high theoretical capacities of promising crystalline network. Three targeted cathode compositions were chosen for the present study ($NaFe_{0.5}(VO)_{0.5}PO_4$, $NaMn_{0.7}(VO)_{0.3}PO_4$ and $NaCo_{0.7}(VO)_{0.3}PO_4$) based on the superior performance over their crystalline counter parts with highest current density ~ 100 mAh/g. XRD results displayed that major crystalline phases ($Na_2FeP_2O_7$ (COD ID: 4001802), $Na_2MnP_2O_7$ (ICSD ID: 71229)) which are precipitated with an ordered triclinic, P1 structure. However, $Na_2CoP_2O_7$ (ICSD ID: 71230) crystalline phase exhibits orthorhombic/P n a 21 structure. The highest conducting glass-ceramic cathode sample $NaCo_{0.7}(VO)_{0.3}PO_4$ ($\sigma = 6.41 \times 10^{-7}$ S·cm^{-1}) retains its discharge capacity retention as 84.5 mAh g^{-1} (91%) even after 50 cycles. At a high rate of 10C, $NaFe_{0.5}(VO)_{0.5}PO_4$ cathode sample is achieved to be highest discharge capacity retention 69.7% than $NaCo_{0.7}(VO)_{0.3}PO_4$ (53.76%) which is a significant feature of mixed polyanion family of glass-ceramic cathodes.

1. Introduction

The Na-ion battery technology has ushered in an alternative pathway to Li-ion battery technology for use in large scale energy storage devices and grid-scale energy storage systems (solar and wind) owing to their significant advantages including cost and natural abundance [1–6]. However, the design of suitable electrode and electrolyte materials with required specific energy capacity and voltage which are yet to be analyzed thoroughly in order to realize viable Na-ion batteries under ambient temperature for the mentioned applications [7]. The fact that cathode capacity plays a significant role in estimating the performance of solid state battery system, extensive research has been conducted on a variety of crystalline structural oxide systems (e.g. Na_xCoO_2, $NaCrO_2$, $NaVO_2$, $Na_x(Fe_{1/2}Mn_{1/2})O_2$) and polyanionic cathodes (e.g. $NaFePO_4$, $Na_3V_2(PO_4)_3$, $NaVPO_4F$, Na_2FePO_4F, $NaFeSO_4F$) in order to realize highly efficient Na-ion batteries even at room temperatures [3,8–14]. Despite their higher efficiency, these crystalline systems suffer with certain deficiencies such as low electrical conductivity and irreversible phase changes during cycling, limiting it from commercialization. Kercher et al. have been published successfully for the first time on structural and electrochemical correlations of mixed polyanion glasses as a function of various polyanion group (borate, molybdate, and vanadate) substitutions to meet above mentioned gaps and limitations [15–17]. Similarly, our research group also focused on variety of mixed polyanion glass and glass-ceramic network systems to overcome the dis-advantages of crystalline networks such as poor electronic conductivity, cycle life and low working voltage where the polyanion content plays a vital role in the $NaM_{1-x}(VO)_xPO_4$ (M = Fe/Co/Mn) (x = 0.1, 0.3, 0.5 and 0.7) glass and glass-ceramic cathode samples in achieving good discharge charge capacity retention even after 50 cycles. The correlations between structural and CV studies of these investigations revealed that $NaFe_{0.5}(VO)_{0.5}PO_4$ (x = 0.5 mol%), $NaMn_{0.7}(VO)_{0.3}PO_4$ (x = 0.3 mol%) and $NaCo_{0.7}(VO)_{0.3}PO_4$ (x = 0.3 mol%) glass-ceramic cathode samples have achieved the best electrochemical performance among all the samples synthesized in the respective series (Fe, Mn and Co) [18].

Owing to the technological significance of mixed polyanion family these glass networks, it is also worth to attempt in this paper to make a comparative analysis of three targeted mixed polyanion glass-ceramic cathode samples $NaFe_{0.5}(VO)_{0.5}PO_4$, $NaMn_{0.7}(VO)_{0.3}PO_4$ and $NaCo_{0.7}(VO)_{0.3}PO_4$ respectively.

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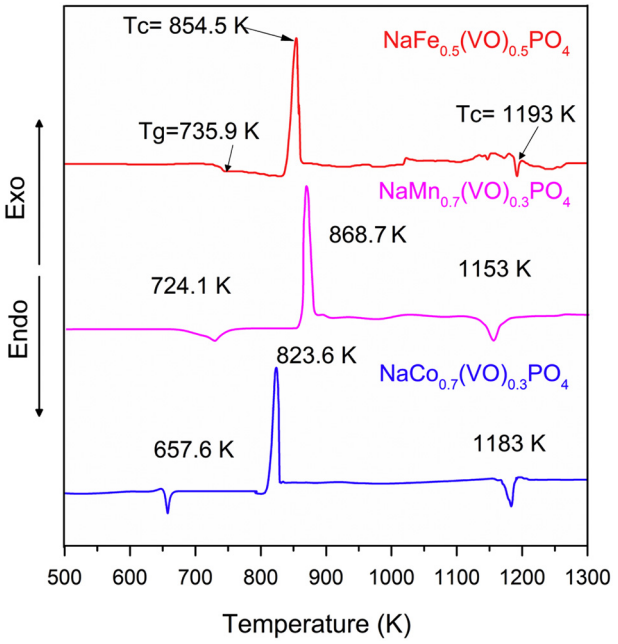

Fig. 1. DTA pattern of $NaFe_{0.5}(VO)_{0.5}PO_4$, $NaMn_{0.7}(VO)_{0.3}PO_4$ and $NaCo_{0.7}(VO)_{0.3}PO_4$ glass powder samples prepared by mechanical milling.

Table 1
Summary of DTA parameters of all mixed polyanion glass-ceramic cathode samples.

Mixed polyanion glass-ceramic cathode	T_g (K)	T_c (K)	T_m (K)	$\Delta T = T_c - T_g$(K)
$NaFe_{0.5}(VO)_{0.5}PO_4$	735.9	854.5	1193	118.6
$NaMn_{0.7}(VO)_{0.3}PO_4$	724.1	868.7	1153	144.6
$NaCo_{0.7}(VO)_{0.3}PO_4$	657.6	823.6	1183	166

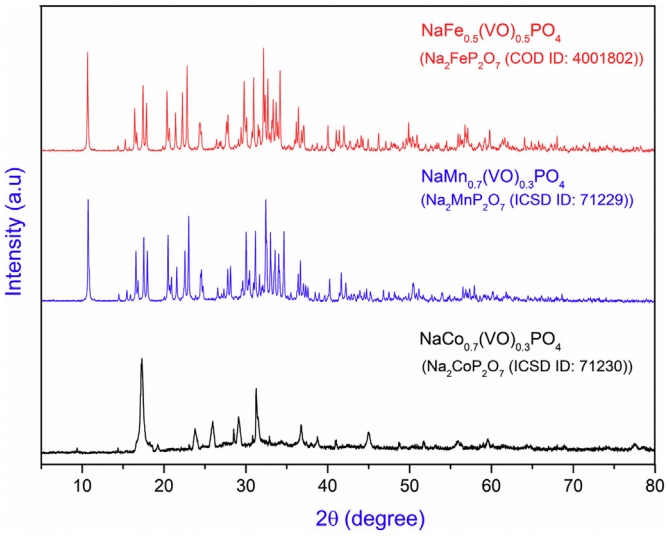

Fig. 2. Powder XRD pattern of $NaFe_{0.5}(VO)_{0.5}PO_4$, $NaMn_{0.7}(VO)_{0.3}PO_4$ and $NaCo_{0.7}(VO)_{0.3}PO_4$ glass-ceramic powder samples.

2. Experimental section

A conventional melt-quenching method was employed to synthesize all the three glass samples ($NaFe_{0.5}(VO)_{0.5}PO_4$, $NaMn_{0.7}(VO)_{0.3}PO_4$ and $NaCo_{0.7}(VO)_{0.3}PO_4$). Stoichiometric ratios of all reagent grades of Na_2CO_3, Fe_2O_3, MnO_2, CoC_2O_4, V_2O_5 and $NH_4H_2PO_4$ were mixed well in an agate mortar and placed in a platinum crucible, the mixtures were melted at 1200 °C in an electric furnace for 30 min. The melts were poured onto an iron plate and pressed to a thickness of 0.5–2 mm by another iron plate. Glass powders were obtained by crushing and grinding bulk glasses using a ball mill for 30 h with 1:10 powder to ball ratio at 250 rpm. Then the precursor glass samples, thus collected were heat treated in 5% H_2–95% Ar atmosphere in a tubular electric furnace at their corresponding crystallization temperatures (T_c) for 5 h, resulting to form their glass-ceramics. Reduced graphene oxide (7 wt%) was added to glass-ceramic powders in order to enhance the conductivity during crystallization. Differential thermal analysis (DTA) of glass-ceramic samples was obtained at a heating rate of 10 K min^{-1}. The crystalline phase present in the glass-ceramic samples were identified by X-ray diffraction (XRD) analyses (Cu Kα radiation) at room temperature. The procedures employed for the half cell configuration and cyclic voltammetric (CV), as discussed in our paper [18].

3. Results and discussions

The glass transition temperature (T_g) and crystallization temperature (T_c) of all the three glass cathode samples is obtained by endothermic dips and exothermic peaks of DTA traces, as depicted in Fig. 1. It could be inferred from the Fig. 1 that the highest thermal stability of glass ($\Delta T = T_c - T_g = 166$ K) is achieved for cobalt based glass-ceramic sample ($NaCo_{0.7}(VO)_{0.3}PO_4$). Crystallization temperature, (T_c) of DTA traces for the possible sodium cobalt pyrophosphate nanocrystalline phases are determined and they have precipitated during the transfer of mixed polyanion glass network in to glass-ceramic. The summary of DTA parameters for the prepared glass-ceramic cathode samples are summarized in the Table 1.

XRD spectra of all the three mixed polyanion glass-ceramic cathodes ($NaFe_{0.5}(VO)_{0.5}PO_4$, $NaMn_{0.7}(VO)_{0.3}PO_4$ and $NaCo_{0.7}(VO)_{0.3}PO_4$) is illustrated in Fig. 2. The presence of peaks that reflects in XRD traces of Fig. 2 is clearly identified with the precipitation of three major crystalline phases. Among them, iron and manganese based crystalline phases $Na_2FeP_2O_7$ (COD ID: 4001802), $Na_2MnP_2O_7$ (ICSD ID: 71229) are observed with an ordered Triclinic, P1 structure and the cobalt based phase $Na_2CoP_2O_7$ (ICSD ID: 71230) exhibited with orthorhombic/P n a 21 structure [19–21]. Rietvelt refinement method is used monitor the structural parameters of as mentioned phases. Further, a secondary phase $NaVO_3$ is also well indexed which doesn't influence on overall electrochemical performance. Structural illustrations of all the three major crystalline phases a) $Na_2FeP_2O_7$ b) $Na_2MnP_2O_7$ and c) $Na_2CoP_2O_7$ can be seen in Fig. 3. Furthermore Crystallite sizes are evaluated by a standard Williamson-Hall (W-H) equation in all the samples where the average crystallite size varies from 118 nm to 217 nm (Fig. 4) [22]. On the other hand, structural parameters are calculated for all the three mixed polyanion glass-ceramic cathodes and also compared with experimental parameters (Table 2).

SEM pictures of all the three glass–ceramic samples are depicted in Fig. 5. SEM images of mixed polyanion glass-ceramic samples ($NaFe_{0.5}(VO)_{0.5}PO_4$, $NaMn_{0.7}(VO)_{0.3}PO_4$ and $NaCo_{0.7}(VO)_{0.3}PO_4$) in Fig. 5 displayed that the major crystalline phases such as $Na_2CoP_2O_7$, $Na_2FeP_2O_7$ and $Na_2MnP_2O_7$ which are embedded with uniform