Journal of Non-Crystalline Solids 450 (2016) 109–115

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Cathode properties of sodium iron phosphate glass for sodium ion batteries

Satoshi Nakata, Takuya Togashi, Tsuyoshi Honma *, Takayuki Komatsu

Department of Materials Science and Technology, Nagaoka University of Technology, Kamitomioka-cho 1603-1, Nagaoka, Niigata 940-2188, Japan

ARTICLE INFO

Article history:
Received 27 May 2016
Received in revised form 21 July 2016
Accepted 3 August 2016
Available online xxxx

Keywords:
Sodium ion batteries
Sodium iron phosphate
Electrical conductivity
Electrochemical properties

ABSTRACT

In order to clarify the possibility of cathode activity of Na_2O-FeO-P_2O_5 glasses for sodium ion batteries, glass formation tendency, crystallization behavior, electrical conductivity as well as charge and discharge properties are examined. Glass formation in xFeO–(100-x)$NaPO_3$ was confirmed for $x \leq 45$ by melt quenching up to 1000 °C in N_2 filled electric furnace. By means of electrical conductivity tests, conductivity was increased with increases of x content in xFeO–(100-x)$NaPO_3$ and the activation energy for electrical conductivity was decreased. Charge and discharge profiles for Na anode exhibits high reversible discharge capacity as 115 mAh/g at 0.1 °C rate in 40FeO-60$NaPO_3$ (30Na_2O–40FeO–30P_2O_5) glass. The results on Raman scattering spectra suggests that glass structure is subjected to polymerized Q^1 and Q^2 phosphate units. And polymerized phosphates in glass cause lower density, open structure and sodium ion diffusive channels as well.

1. Introduction

Li-ion batteries (LIB) have been intensively developed after the first launch of the Li-ion batteries in 1990s. LIBs are essential for the development of smart phones, laptop computers, and many other consumer products these days. The next targets of LIBs are considered to be automotive applications and huge energy storage systems. The materials abundance is of the primary importance to design the electrode materials for such large-scale applications. Sodium ion batteries are focused as alternative secondary batteries to save material cost recently [1]. Due to the intensive research, the energy density of the sodium ion battery is increasingly become equal to that of conventional LIBs [2]. In cathode, layer rock salt type oxides as well as poly-anion type materials are considered as active materials in recently.

Triclinic $P\bar{1}$ $Na_2FeP_2O_7$ exhibits 3.0 V, 97 mAh/g with good cyclic performance [3–7]. $Na_2FeP_2O_7$ is also available in aqueous based sodium ion batteries that implies chemical stability is good [8]. The authors group is proposing unique technique to produce $Na_2FeP_2O_7$ by crystallization of precursor glass so-called 'glass-ceramic process', which is also applicable to fabricate $LiFePO_4$, $LiMn_xFe_{1-x}PO_4$ and $Li_3V_2(PO_4)_3$ as well in our previous study [9–11]. By means of transmission electron microscope observation, there are residual amorphous phase on the surface of glass-ceramic grain.

Nagakane et al. [11] are proposing that residual amorphous is effective to assist ionic conduction in $LiFePO_4$ cathode, which exists only one-dimensional Li^+ diffusive channel. On the other hand, to improve capacity of materials is another important point to achieve high energy density. As shown in Fig. 1 there are five crystals are found in ternary $NaO_{0.5}$-FeO$_x$-$PO_{2.5}$ systems. To focus on sodium pre-doped Fe^{2+} base crystal, there are three candidates, $Na_2FeP_2O_7$, $Na_4Fe_3(PO_4)_2P_2O_7$ and maricite type $NaFePO_4$ are remained [12,13]. Comparing with theoretical capacity, unfortunately, $NaFePO_4$, which is stoichiometric composition of olivine type $LiFePO_4$, is inactive for sodium cell cathodes. Isolated PO_4 units are exist periodically and they are blocking Na^+ ion diffusion in maricite structure.

On the other hand, the amorphous material like glass has the random three-dimensional structure. It is known that glass have large free volume and flexible open structure, hence superior alkali ion conduction exhibits in glass-ceramic derived solid state electrolytes for lithium ion batteries and sodium ion batteries as well [14,15]. It is not unique to solid electrolyte, there are possibility to develop for cathode and anode active materials. Okada et al. suggests that mechano-chemical derived amorphous $FePO_4$ have a corner-shared matrix, and they showed similarly good capacity, not only for Li but also for Na anodes [16,17]. SnO-P_2O_5 glass is also available as anode active materials in Li and Na cell [18–20]. It would be interesting to examine the nature of ionic conduction of glassy state cathode materials such as Na_2O-FeO-P_2O_5 system. In this study, glass formation tendency, electrical conductivity and cathode activities of sodium iron phosphate glasses are examined for sodium ion batteries.

2. Experimental procedure

The glass composition examined in this study is xFeO–(100-x)$NaPO_3$ (x = 20, 25, 33.3, 40, 45 and 50). Fig. 1 shows glass formation region

* Corresponding author.
E-mail address: honma@mst.nagaokaut.ac.jp (T. Honma).

http://dx.doi.org/10.1016/j.jnoncrysol.2016.08.005
0022-3093/

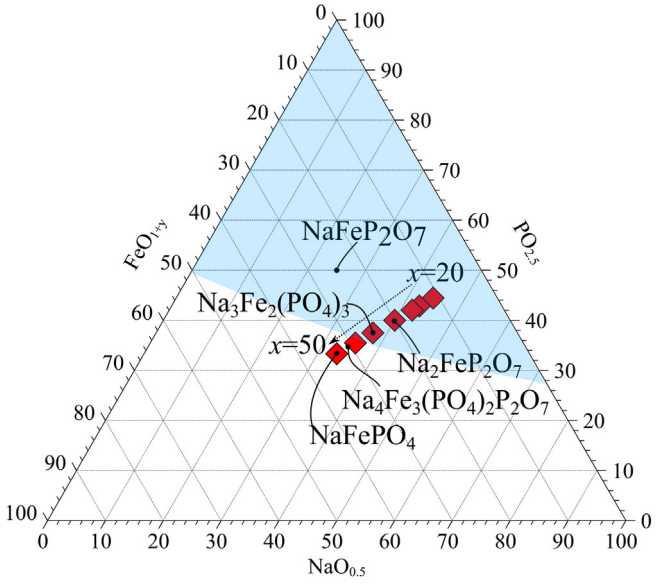

Fig. 1. Glass formation region and examined glass compositions in $NaO_{0.5}$-$FeO_{1+\delta}$-$PO_{2.5}$ systems. We also added typical crystals ever reported.

which is determined by INTERGLAD (glass database) with light blue [21] and illustrated sample composition as red mark. In these glasses there are three stoichiometric compositions of $Na_2FeP_2O_7$ ($x = 33.3$), $Na_3Fe_2(PO_4)_3$ ($x = 40$) and $NaFePO_4$ ($x = 50$). The fraction of Fe^{2+} ions in an Na_2O-Fe_2O_3-P_2O_5 glass varies with the initial batch materials and preparation conditions, initial fraction of raw materials. In generally, the fraction of Fe^{2+} increase when ferrous raw materials are used such as FeO, Fe_3O_4 rather than Fe_2O_3 and when melts are processed under reducing conditions [22,23]. When the melting is process under atmosphere the fraction of Fe^{2+} is about up to 20%. In this study we are expecting to develop Na^+ pre-doped cathode, therefore the fraction of Fe^{2+} must be high. Glasses were fabricated by a conventional melt-quenching method under reducing atmosphere. Starting reagents NaH_2PO_4 (99%, Nakarai tesque Co.), FeO (99.9%, Kojyundo chemicals Co.) were mixed well. A 20 g batch was melted in a gold crucible at 900 °C for 15 min in flowing N_2 gas (5 L/min) in muffle furnace. The melts were poured onto an iron plate and pressed to a thickness of 0.5–1 mm by another iron plate. The glass transition and crystallization temperatures were determined by differential thermal analysis (DTA, Rigaku TG-8120). In order to confirm glass formation and to characterize crystallized phase, XRD patterns of all samples were obtained on Rigaku Ultima IV X-ray diffractometer (Rigaku, Japan) with D/tex 1D high-speed detector, which was operated at 40 kV, 40 mA with Cu-Kα radiation ($\lambda = 0.154056$ nm). All the measurements were carried out at room temperature under atmospheric air. Raman spectra were recorded using a Nanofinder (Tokyo Instruments, Japan) confocal Raman with Ar laser beam having a wavelength of 488 nm using a CCD detector. Electrical conductivities of glasses were measured by an alternating current (AC) impedance method (HIOKI 3522-50 LCR HiTESTER, Japan) in the temperature range from room temperature to 200 °C. Metal gold was sputtered with 6.5 mmϕ to the glass surface as electrodes (ULVAC QUICK COATER VPS-020, Japan).

Pre-pulverized glass flake obtained by automatic mortar was subjected to mechanical milling in a planetary ball mill (Fritsch Premium line Pulversette No. 7). The following milling conditions were used: air atmosphere; milling speed of 600 rpm; ball to powder mass ratio of 10:1; and milling time of 1 h. In order to avoid excessive temperature rising within the grinding chamber, 15 min of ball milling duration was followed by a pause of 5 min. Composite powder was classified by sieving to the size of <15 μm. Morphologies of glass-ceramics/carbon composites were observed by scanning electron microscope (SEM, Keyence VE-8800).

Cathode electrodes were fabricated from a mixture of glass powder, polyvinylidene fluoride (PVDF) and conductive carbon black in a weight ratio of 85:5:10. N-methylpyrrolidone (NMP) was used to make slurry

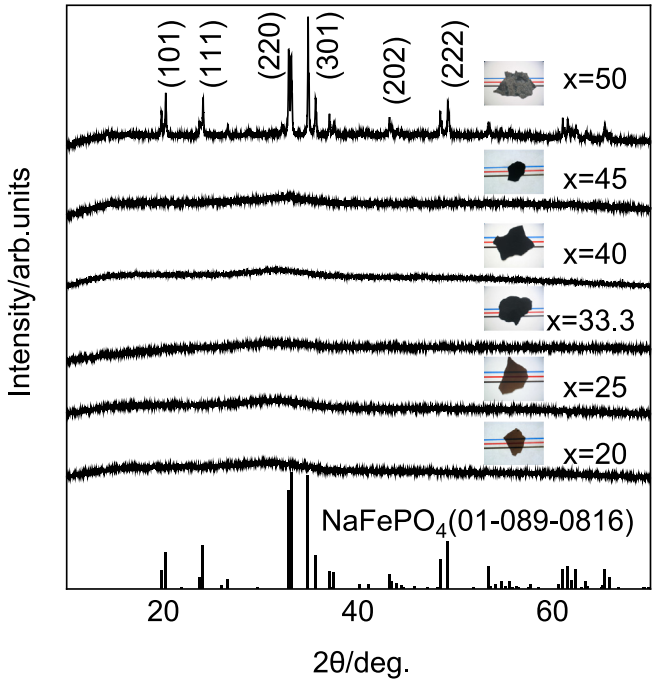

Fig. 2. Powder XRD patterns of xFeO–(100-x)$NaPO_3$ ($x = 20$, 25, 33.3, 40, 45 and 50).

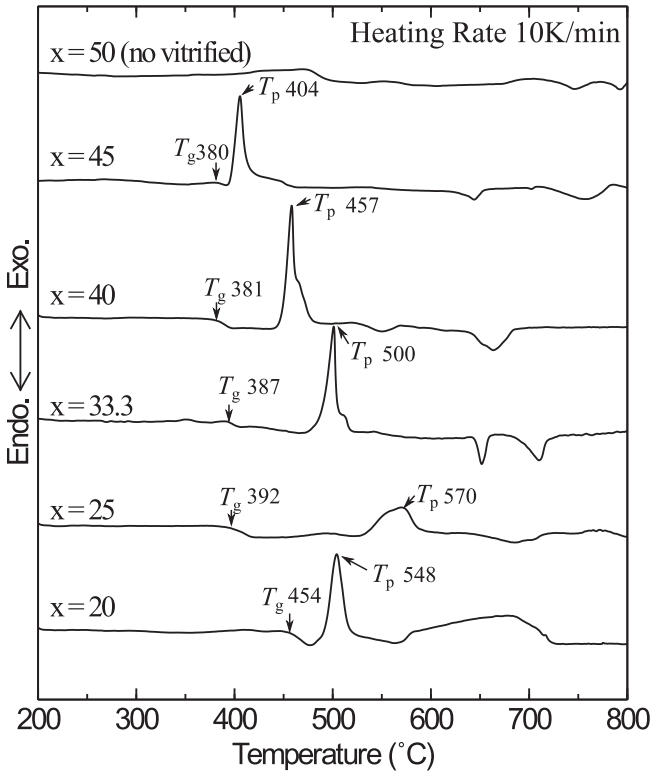

Fig. 3. DTA profiles of quenched samples of xFeO–(100-x)$NaPO_3$ ($x = 20$, 25, 33.3, 40, 45 and 50).