

## Mössbauer study of new vanadate glass with large charge-discharge capacity

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**Abstract** Charge-discharge capacity and cyclicity of lithium ion battery (LIB) was evaluated in which  $15\text{Li}_2\text{O} \cdot 10\text{Fe}_2\text{O}_3 \cdot x\text{SnO}_2 \cdot 5\text{P}_2\text{O}_5 \cdot (70-x)\text{V}_2\text{O}_5$  glass ( $x = 0$  and  $20$  in mol%, abbreviated as  $x\text{LFSPV}$ ) was used as a cathode. A local structure of  $x\text{LFSPV}$  glass before and after charging was investigated by  $^{57}\text{Fe}$ - and  $^{119}\text{Sn}$ -Mössbauer spectroscopies.  $^{57}\text{Fe}$ -Mössbauer spectrum of  $x\text{LFSPV}$  glass with ‘ $x$ ’ of  $20$  was composed of a doublet with isomer shift ( $\delta$ ) of  $0.35_{\pm 0.02} \text{ mm s}^{-1}$  and quadrupole splitting ( $\Delta$ ) of  $0.88_{\pm 0.03} \text{ mm s}^{-1}$  due to distorted  $\text{Fe}^{\text{III}}\text{O}_4$  tetrahedra.  $^{119}\text{Sn}$ -Mössbauer spectrum of this glass consisted of a doublet with  $\delta$  of  $0.08_{\pm 0.01}$  and  $\Delta$  of  $0.52_{\pm 0.01} \text{ mm s}^{-1}$  due to distorted  $\text{Sn}^{\text{VI}}\text{O}_6$  octahedra. After discharging the battery from  $4.5$  to  $1.0$  V, larger  $\delta$  of  $0.40_{\pm 0.03} \text{ mm s}^{-1}$  and  $\Delta$  of  $0.94_{\pm 0.04} \text{ mm s}^{-1}$  were obtained, indicating that both ionicity of Fe-O bonds and local distortion of  $\text{Fe}^{\text{III}}\text{O}_4$  tetrahedra were increased. On the contrary, identical  $\delta$  of  $0.09_{\pm 0.01} \text{ mm s}^{-1}$  and  $\Delta$  of  $0.50_{\pm 0.01} \text{ mm s}^{-1}$  were observed in the  $^{119}\text{Sn}$ -Mössbauer spectrum of  $20\text{LFSPV}$  glass after the discharge,

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indicating that chemical environment of  $\text{Sn}^{\text{IV}}\text{O}_6$  octahedra was not affected after the discharge. Charge-discharge curve of LIB containing 20LFSPV glass as a cathode active material recorded under the current density of  $8.3 \text{ mA g}^{-1}$  ( $0.011 \text{ mA cm}^{-2}$ ) between 1.0 and 4.5 V showed a large initial charge capacity of  $431.1 \text{ mAh g}^{-1}$  and discharge capacity of  $382.3 \text{ mAh g}^{-1}$ , respectively. These results indicate that 20LFSPV glass could be a new cathode active material for LIB.

**Keywords** Cathode active material · Lithium ion battery · Charge-discharge capacity ·  $^{57}\text{Fe}$ -Mössbauer spectroscopy ·  $^{119}\text{Sn}$ - Mössbauer spectroscopy

## 1 Introduction

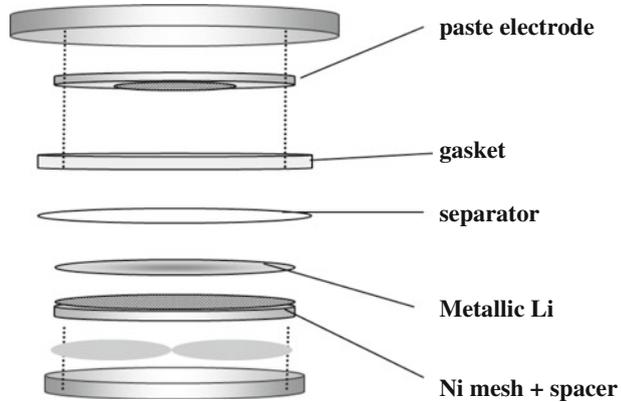
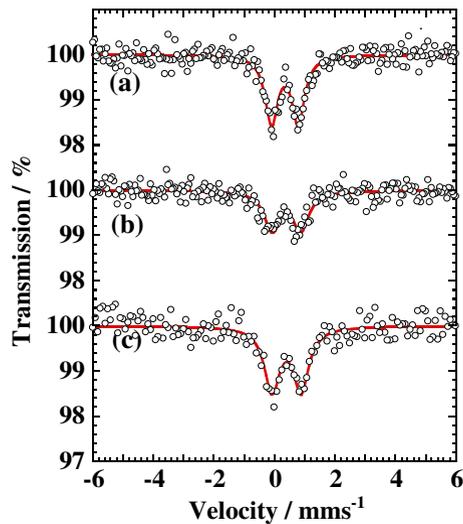
Vanadate glass exhibits high electrical conductivity ( $\sigma$ ) of  $10^{-7}$ – $10^{-5} \text{ Scm}^{-1}$  due to small polaron hopping between  $\text{V}^{\text{IV}}$  and  $\text{V}^{\text{V}}$  [1]. It proved that conductivity of  $\text{BaO}\cdot\text{Fe}_2\text{O}_3\cdot\text{V}_2\text{O}_5$  glass was increased by a factor of  $10^5$ – $10^6$  due to structural relaxation of glass-network, caused by isothermal annealing at a given temperature higher than glass transition temperature ( $T_g$ ) or crystallization temperature ( $T_c$ ) [2]. For example,  $x\text{BaO}\cdot(90-x)\text{V}_2\text{O}_5\cdot 10\text{Fe}_2\text{O}_3$  glass showed a remarkable increase of  $\sigma$  up to  $10^0 \text{ Scm}^{-1}$  as a result of the structural relaxation [3]. This unique electrical property of vanadate glass could be applied to the cathode active material,  $\text{LiFeVPO}_x$ , of lithium ion battery (LIB) [4]. Kubuki et al. revealed that isothermal annealing of  $15\text{Li}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot 20\text{SnO}_2\cdot 5\text{P}_2\text{O}_5\cdot 50 \text{V}_2\text{O}_5$  glass resulted in a remarkable increase of  $\sigma$  to the order of  $10^{-2} \text{ Scm}^{-1}$  [5, 6]. In this study, local structural change of vanadate glass developed as a new cathode active material was investigated by  $^{57}\text{Fe}$ - and  $^{119}\text{Sn}$ - Mössbauer spectroscopies, caused by charge and discharge of LIB.

## 2 Experimental

New vanadate glasses,  $15\text{Li}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{SnO}_2\cdot 5\text{P}_2\text{O}_5\cdot (70-x)\text{V}_2\text{O}_5$ , abbreviated as  $x\text{LFSPV}$  ( $x = 0$  and  $20$  in mol%) were prepared by a conventional melt-quenching method. Weighed amounts of  $\text{Li}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{V}_2\text{O}_5$  of reagent grade were melted at  $1200 \text{ }^\circ\text{C}$  for 1 h in an electric muffle furnace.  $^{57}\text{Fe}$ - and  $^{119}\text{Sn}$ -Mössbauer spectra were measured by a constant acceleration method at room temperature with a source of  $^{57}\text{Co}$  (Rh) or  $\text{Ca}^{119\text{m}}\text{SnO}_3$  and a reference of  $\alpha\text{-Fe}$  foil or  $\text{BaSnO}_3$ . As shown in Fig. 1, LIB was prepared by using 2032 type coin cell composed of  $x\text{LFSPV}$  glass, metallic Li, and 1 M  $\text{LiPF}_6$  diffused into a mixture of ethylene carbonate + dimethyl carbonate mixture (1:1) as cathode, anode and electrolyte, respectively. Charge-discharge capacity was monitored under a current density and voltage range of  $8.3 \text{ mA g}^{-1}$  ( $0.011 \text{ mA cm}^{-2}$ ) and 1.0–4.5 V, respectively.

## 3 Results and discussion

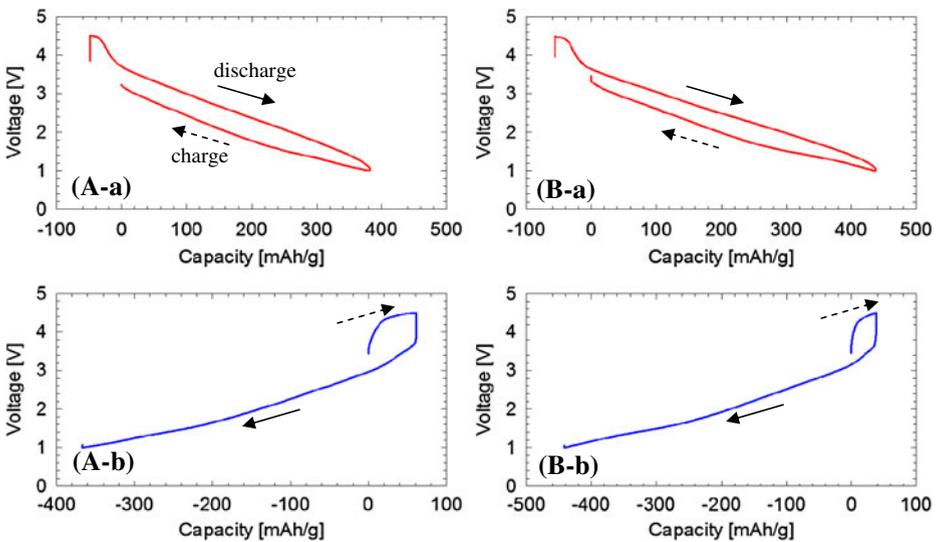
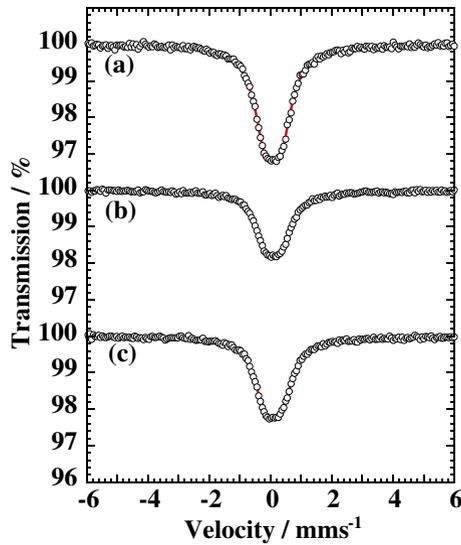
$^{57}\text{Fe}$ -Mössbauer spectra of 20LFSPV glass measured before and after charging the coin cell are shown in Fig. 2. Before discharging,  $^{57}\text{Fe}$ -Mössbauer spectrum composed of a paramagnetic doublet with isomer shift ( $\delta$ ) of  $0.35_{\pm 0.02} \text{ mm s}^{-1}$  and quadrupole

**Fig. 1** Set-up of Li-ion coin cell**Fig. 2**  $^{57}\text{Fe}$ -Mössbauer spectra of 20LFSPV glass utilized for cathode active material of LIB, measured **a** before discharge, **b** after discharge and **c** after re-charge

splitting ( $\Delta$ ) of  $0.88_{\pm 0.02} \text{ mm s}^{-1}$  due to  $\text{Fe}^{\text{III}}\text{O}_4$  distorted tetrahedra. These parameters indicate that iron(III) plays a role of network former (NWF) by sharing corner oxygen atoms with distorted  $\text{VO}_4$  tetrahedra. Larger  $\delta$  of  $0.40_{\pm 0.03} \text{ mm s}^{-1}$  and  $\Delta$  of  $0.94_{\pm 0.04} \text{ mm s}^{-1}$  were observed in  $^{57}\text{Fe}$ -Mössbauer spectrum of 20LFSPV glass after discharging, indicating that both the ionicity of  $\text{Fe}^{\text{III}}\text{-O}$  bond and local distortion of  $\text{Fe}^{\text{III}}\text{O}_4$  were increased. Increases in  $\delta$  from  $0.35_{\pm 0.02}$  to  $0.43_{\pm 0.02}$  and  $\Delta$  from  $0.81_{\pm 0.03}$  to  $0.92_{\pm 0.03} \text{ mm s}^{-1}$  were respectively observed for 0LFSPV after discharging. Being different from the case of  $\text{LiFeVPO}_x$  glass, in which iron changed its valency from  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$  after discharging and from  $\text{Fe}^{\text{II}}$  to  $\text{Fe}^{\text{III}}$  after charging the LIB [4], no change was observed in the present system.

In the  $^{119}\text{Sn}$ -Mössbauer study, broad “singlet” was observed with identical  $\delta$  of  $0.08_{\pm 0.01} \text{ mms}^{-1}$  and  $\Delta$  of  $0.52_{\pm 0.01} \text{ mms}^{-1}$  were observed in all the samples, irrespective of the charge-discharge process, as shown in Fig. 3. This result indicates that tin was incorporated in the form of  $\text{Sn}^{\text{IV}}\text{O}_6$  as a network modifier (NWM),

**Fig. 3**  $^{119}\text{Sn}$ -Mössbauer spectra of 20LFSPV glass utilized for cathode active material of LIB, measured **a** before discharge, **b** after discharge and **c** after re-charge

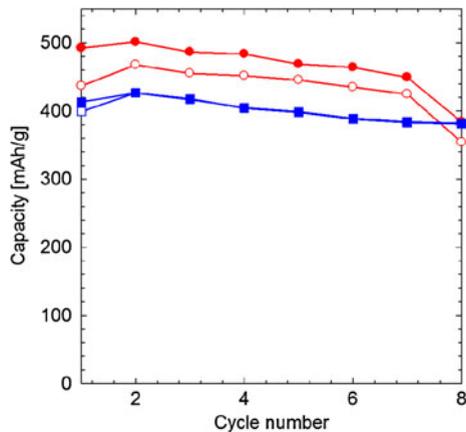


**Fig. 4** Charge-discharge curve of LIB containing  $x$ LFSPV glass with ' $x$ ' of (A) 20 and (B) 0 as a cathode active material, started recording with **a** discharge and **b** charge processes under current density and applied voltage of  $8.3 \text{ mA g}^{-1}$  ( $0.011 \text{ mA cm}^{-2}$ ) and 1.0–4.5 V, respectively

and that the chemical environment was scarcely affected during the charge-discharge process.

Charge-discharge profiles of LIB containing 20LFSPV glass as a cathode material is illustrated in Fig. 4. A large initial charge capacity of  $431.1 \text{ mAh g}^{-1}$  and a large initial discharge capacity of  $382.3 \text{ mAh g}^{-1}$  were recorded when the measurement was initiated from discharging process (Fig. 4(A-a)), while a small initial charge

**Fig. 5** Cyclicality of LIB containing  $x$ LFSPV glass with ' $x$ ' of 0 (*circle*) and 20 (*square*) as a cathode active material, recorded under discharging (*open symbol*) and recharging (*solid symbol*) at the current density and applied voltage of  $8.3 \text{ mA g}^{-1}$  ( $0.011 \text{ mA cm}^{-2}$ ) and 1.0–4.5 V, respectively



capacity of  $61.2 \text{ mAh g}^{-1}$  and an initial discharge capacity of  $428.3 \text{ mAh g}^{-1}$  were recorded when started from charging process (Fig. 4(A-b)). It is noted that the capacity was slightly larger when 0LFSPV glass was used as a cathode active material (Fig. 4(B-a) and (B-b)), and that a flat charging line to  $V^{IV}$  or  $V^V$  was observed at the vicinity of 3.5 V in the charge-discharge curve was initiated from charging process (Fig. 4(A-b) and (B-b)). As compared with the charge capacity reported for non-annealed and annealed LIB containing LFVPO<sub>x</sub> glass, i.e., 50 and  $150 \text{ mAh g}^{-1}$  recorded under a current density of  $0.1 \text{ mA cm}^{-2}$  and a voltage at 2.0 V [4], the larger capacity of  $260 \text{ mAh g}^{-1}$  at 2.0 V during discharge process and of  $160 \text{ mAh g}^{-1}$  at 2.0 V during charge process were recorded for LIB in which 20LFSPV glass was used as a cathode active material (see Fig. 4(A-a)). Larger capacities of  $300 \text{ mAh g}^{-1}$  and  $200 \text{ mAh g}^{-1}$  at 2.0 V were also recorded for the charge-discharge curve of LIB in which 0LFSPV was contained as a cathode active material during discharge and charge process, respectively (see Fig. 4(B-a)). Therefore, it can be said that we could develop  $x$ LFSPV as new cathode active material with higher capacity.

Cyclicality of the LIB containing  $x$ LFSPV glass as the cathode active material is shown in Fig. 5. A stable capacity of about  $400 \text{ mAh g}^{-1}$  was repeatedly recorded when 20LFSPV glass was used as a cathode material (Fig. 5, blue square). Although capacity of LIB containing 20LFSPV glass is smaller than that containing 0LFSPV glass, the former shows higher stability of cyclicality than the latter. This result indicates that tin ions in  $x$ LFSPV glass stabilize the charge-discharge performance of Li-coin cell. It is expected that LIB with higher charge capacity could be achieved when annealed 20LFSPV glass was utilized as a cathode active material because of the larger electrical conductivity of  $10^{-2} \text{ Scm}^{-1}$  [5]. These results prove that  $x$ LFSPV glass will be applied as a cathode active material for LIB with higher performance.

#### 4 Summary

A relationship between local structure and charge-discharge performance of LIB containing  $x$ LFSPV glass as a cathode active material was evaluated by  $^{57}\text{Fe}$ - and  $^{119}\text{Sn}$ -Mössbauer spectroscopies. Increases in  $\delta$  from  $0.35_{\pm 0.02}$  to  $0.40_{\pm 0.03} \text{ mms}^{-1}$

and that in  $\Delta$  from  $0.88_{\pm 0.02}$  to  $0.94_{\pm 0.04}$   $\text{mm s}^{-1}$  obtained in 20LFSPV glass after discharging LIB reveals an increased ionicity of Fe-O bonds and also increased local distortion of  $\text{Fe}^{\text{III}}\text{O}_4$  units. In contrast, constant  $\delta$  of  $0.08_{\pm 0.01}$   $\text{mms}^{-1}$  and  $\Delta$  of  $0.52_{\pm 0.01}$   $\text{mms}^{-1}$  were observed in  $^{119}\text{Sn}$ -Mössbauer spectra after discharging LIB, indicating that  $\text{Sn}^{\text{IV}}\text{O}_6$  octahedra in 20LFSPV glass showed little change of the chemical environment. A large charge capacity of  $431.1 \text{ mAh g}^{-1}$  was recorded in a charge-discharge curve of LIB in which 20LFSPV glass was utilized as a cathode active material. It is expected that new LIB could be prepared using 20LFSPV glass as a cathode active material.

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