The Formation of an Ionically Conducting Surface Layer on a $50\text{V}_2\text{O}_5 - 50\text{TeO}_2$ Glass by the Electrochemical Lithiation

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By the electrochemical lithiation of an electronically conducting $\text{V}_2\text{O}_5\text{-TeO}_2$ (50–50 mol%) glass in a LiClO_4 –propylene carbonate solution, an ionically conducting surface layer was formed. The e.m.f. of a solid state cell

$\text{Li} \mid \text{surface layer} \mid 50\text{V}_2\text{O}_5\text{-}50\text{TeO}_2 \text{ glass}$
was stable at > 2.4 V over a few months, which verified the presence of this layer having a predominant Li^+ ion conductivity compared with the electronic conductivity.

1. INTRODUCTION

So far, the application of some amorphous transition metal chalcogenides for a positive pole material in lithium batteries was described in several reports [1–6].

In a series of our electrochemical studies on transition metal oxide glasses, the electrochemical insertion of lithium into $\text{V}_2\text{O}_5\text{-TeO}_2$ glass thin (ca. 20 μm) films was investigated by a galvanostatic intermittent titration technique [7, 8] and we observed that the minimum point appears on the o.c.v. vs. mean (Li/V) composition curve only when a high current density is employed for the lithiation.

Most likely, this phenomenon results from the supersaturation of inserted lithium in a glass matrix before the nucleation of a new phase being either crystalline or amorphous. Sakurai *et al.* [4] investigated the discharge/charge cycling of $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ glasses in a secondary lithium cell, on the other hand, and found that a certain portion of inserted lithium can not be extracted on charging. We are suspecting that unrechargeable lithium in this $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ glass is also closely related to the above phase separation phenomenon triggered by a given Li^+ ion flux.

In this paper, the formation of a Li^+ ion conducting surface layer on a $50\text{V}_2\text{O}_5\text{-}50\text{TeO}_2$ glass by the electrochemical lithium insertion will be evidenced on a basis of the e.m.f. measurement of a solid state cell

$\text{Li} \mid \text{surface layer (I-phase)} \mid$

$50\text{V}_2\text{O}_5\text{-}50\text{TeO}_2 \text{ glass (E-phase)} \quad (1),$

where I- and E-phases represent ionic and electronic conductors, respectively. Strictly, the former may be a mixed conductor.

2. EXPERIMENTAL

2.1 $50\text{V}_2\text{O}_5\text{-}50\text{TeO}_2$ glass electrodes

Equal moles of V_2O_5 (purity $> 99.5\%$) and TeO_2 (purity $> 99\%$) powders were melted in a sintered alumina crucible at 800°C for 30 min, where the melt was mixed up after every 5 min to prevent separation of the two components. Then the melt was quenched on a stainless steel plate preheated at 170°C . The obtained glass ingot was annealed at 180°C for 300 min to release the internal stress. These procedures were carried out under air atmosphere.

In a X-ray powder diffraction pattern, any sharp line other than a broad hallow at around 25° (2θ , $\text{CuK}\alpha$) could not be observed. The d.c. conductivity determined at room temperature by using two vacuum deposited gold electrodes was $1.6 \times 10^{-7} \text{ S cm}^{-1}$ with a perfectly electronic nature. This value is somewhat smaller than a literature [9] data, $3.2 \times 10^{-6} \text{ S cm}^{-1}$, owing to the possible slight difference in quenching and/or annealing conditions.

The ingot was sliced by a diamond wheel to several thin (ca. 0.5 mm) plates of which both faces were polished with emery papers up to #2000. Two segments facing to atmosphere and to a quenching substrate were wasted because of the possible contamination. The glass plate was mounted in poly(ester) resin after connect-

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ing with a copper wire through a deposited gold layer on the back face. Finally, a thin lead wire was bonded on a edge of the front face (ca. 0.2 cm^2) for the IR-free potential measurements.

2.2 Electrochemical insertion of lithium

A glass electrode was polarized cathodically in a 1 mol dm^{-3} LiClO_4 -propylene carbonate (PC) solution as in a previous work [7], where a triangular controlled current ($0 \sim -2.5 \text{ A m}^{-2}$, 2.1 mHz) was applied continuously at various temperatures.

2.3 Solid state cells

The surface of a lithiated glass was wiped carefully and then contacted with lithium (purity $> 99.8\%$) polished to metallic brightness, by which a cell of eq.(1) was constructed. The solid state cell was stored in silicone oil after sealing with a resin. These procedures were carried out in a dry box under argon atmosphere.

The cell e.m.f. was measured by a digital voltmeter (input impedance $> 10^{12} \Omega$). The galvanostatic polarization of a solid state cell was studied by a high precision potentio/ galvanostat (Toho Giken, Model 2092).

3. RESULTS AND DISCUSSION

3.1 Electrochemical insertion of lithium

Figure 1 shows typical changes in the lithiating potential (IR-free) with cycle numbers of controlled-current reduction. Curves 1 and 2 correspond to potentials at the minimum and the maximum levels of an applied triangular current, respectively. If we assume that the rate of lithiation is controlled by the transport of lithium in the glass phase, the lower lithiating potential corresponds to the higher concentration of lithium at the glass surface. Hence, the inflection points on these curves are considered to correspond to drastic increases in the surface concentration of lithium which may result in the nucleation of a lithium-containing new phase.

Furthermore, when we assume that an equal amount of Li^+ ions and electrons are injected simultaneously and that inserted lithium is spread over an entire volume of a sample glass plate, then the concentration of lithium is calculated to be $(\text{Li}/\text{V}) = \text{ca. } 0.011$ at the end of the 20 th cycle, for example. The latter assumption, however, is invalid, since lithium is more con-

Fig. 1 Changes in lithiating potentials with controlled-current cyclings at 80°C (see text)

centrated in a surface layer than in a matrix E -phase as described below.

3.2 E.m.f. of a solid state cell

The e.m.f. of a typical solid state cell (1) at 25°C , $U_{1,298\text{K}}$, was plotted in Fig. 2 against a storage time. A similar cell constructed with a glass plate, which was immersed in the electrolyte solution but not lithiated at least by the externally applied current, was confirmed to show no e.m.f. (curve 2). The steady-state e.m.f. on curve 1 demonstrates clearly that there exists an I -phase stably for months of period between two electronically conducting phases of lithium and the mother glass, which is formed by the preceding lithium insertion.

Here, the I -phase is not necessarily a true ionic conductor but can also have a partial electronic conductivity. Since the morphology of a lithiated surface is unknown at present, furthermore, it may be possible generally that the new I -phase does not separate completely the mother glass from a lithium electrode. In the following discussion on the e.m.f. of a solid state cell, the presence of the needle-like direct electron flow paths between lithium and the E -phase is excluded as an assumption.

As can be seen in Fig. 3, $U_{1,298\text{K}}$ increases with a descending temperature (T_{Li}) or with an

Fig. 2 E.m.f. of a solid state cell (1) at 25 °C as a function of a storage time

- 1; lithiation at 25 °C, 8.8 C cm⁻²
2; immersed without external lithiating current

Fig. 3 Changes in e.m.f. of a solid state cell (1) with operating conditions of lithium insertion

- 1; Q_{Li} is constant at 8.8 C cm⁻²
2; T_{Li} is constant at 40 °C

increasing amount of electricity (Q_{Li}) during the lithiation. These results suggest that a transport number of electrons, t_e , in the surface I -layer becomes smaller, or in other words, the solid state cell (1) is short-circuited less markedly by the internal electron flow through a surface layer with the above operating conditions for lithium insertion.

According to Weppner *et al.* [10], t_e is given by

$$t_e = 1 - (U_1 / U_{\text{theor.}}) \quad (2),$$

where $U_{\text{theor.}}$ is a theoretical cell voltage observed for a perfectly ionic conductor ($t_e = 0$). By replacing $U_{\text{theor.}}$ with the open-circuit voltage of an analogous wet cell employing a 1 mol dm⁻³ LiClO₄-PC solution as the electrolyte, 3.3 ~ 3.5 V (298 K) [7], the value of t_e in the formed surface I -layer is estimated to be about 0.2 ~ 0.3.

The positive temperature coefficient of U_1 (ca. +1.5 mV K⁻¹ at 303 K) may suggest that the predominance of the Li⁺ ion conductivity in the I -phase becomes more remarkable with elevating temperature.

3.3 Polarization of a solid state cell

Fig. 4 Galvanostatic micro-polarization tests of a solid state cell at 25 °C

- lithiation at 25 °C, 13.3 C cm⁻²
1; discharging, -50 nA cm⁻²
2; charging, +50 nA cm⁻²

To ensure the reversibility of a solid state cell, micro-polarization tests have been carried out. As seen in Fig. 4, the cell voltage decreases and increases linearly with the square root of a time during discharging and charging current pulses, respectively.

Further, the recuperation after these pulses is also a linear function of the square root of a time. These results show that the applied current pulse is consumed not capacitively but by a faradaic reaction in a solid state cell. It is not yet clear whether the polarization of a solid state cell, probably controlled by a diffusion process, is attributed mainly to the *I*-phase or *E*-phase.

4. CONCLUSION

The formation of an ionically conducting surface layer on a $50V_2O_5$ - $50TeO_2$ glass by the electrochemical lithiation in a $LiClO_4$ - propylene carbonate solution was verified by the steady-state e.m.f. of a solid state cell (1). The coulombic efficiency for the discharge / charge cycling of this glass in a wet lithium cell is considered to be lowered by this phenomenon.

A preliminary X-ray diffraction survey revealed that the formed surface layer has no definite crystalline structure. The chemical composition, the structure, the electrical properties *etc.* of this layer should be investigated in further studies.

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