The Electrochemical Lithium Insertion into $50V_2O_5 - 50TeO_2$ Glass Thin Plates
Takashi MIURA*, Eiji NODA and Tomiya KISHI
Received February 2, 1989 ; Accepted March 16, 1989

The electrochemical insertion of lithium into $V_2O_5 - TeO_2$ (50–50 mol%) binary glass thin (20 μm) plates has been investigated by the galvanostatic intermittent titration technique in a propylene carbonate solution at 25 °C. The chemical diffusion coefficient of lithium in this electronically conducting glass was of the order of $10^{-12}$ cm$^2$ s$^{-1}$ in a range of the lithium content $x$ (Li / V, atomic ratio) up to 0.01.

1. INTRODUCTION
In recent years, the application of some non-crystalline transition metal chalcogenides to a positive pole material in secondary lithium batteries has attracted much attention as reviewed briefly in a previous paper [1].

The transport of Li$^+$ ion in a solid phase probably plays the most dominant role in the kinetics of discharging and charging reactions, where Li$^+$ is inserted to and extracted from a solid active material, respectively. Hence, to evaluate such battery materials, it is necessary to investigate how fast Li$^+$ ion is transported in them in addition to the reversibilities of the potential and of the structural change during discharge-charge cyclings.

In this work, the electrochemical insertion of lithium into an electronically conducting oxide glass in the $V_2O_5 - TeO_2$ binary system [2] has been studied by the galvanostatic intermittent titration technique (GITT) [3], using thin plate electrodes to eliminate complexities originating from the indefinite solid-electrolyte interface geometry and from the intergranular diffusion. The chemical diffusion coefficient of a Li$^+$ ion – electron couple, $D_{Li}$, and related quantities were determined as functions of the lithium concentration in this binary glass.

2. EXPERIMENTAL
2.1 Preparation of glass thin plates
Equal moles of reagent grade $V_2O_5$ and $TeO_2$ powders (both from Soekawa Chemicals) were melted at 800 °C for 30 min in an alumina crucible, where the melt was mixed up after every 5 min to prevent separation of the two components. A portion of the melt was quenched on the edge of a quartz tube by blowing air through this tube. The obtained glass balloon, which was distorted immediately by pressing onto an aluminium plate preheated at 120 °C, was annealed at 180 °C for 300 min and then crushed to thin platelets. The samples were annealed again at 120 °C for 120 min after depositing a gold layer by vacuum evaporation. The thickness of a glass plate measured by an optical dial gauge was ca. 20 μm.

The thermogravimetric analysis up to the melting point showed the presence of an oxygen deficiency in this glass, where about 6% of total vanadium ion was considered to be $4+$ valent. In a X-ray powder diffraction pattern of this glass, a broad hallow having a peak at $2θ = 28°$ (CuKα) appeared, whereas no sharp diffraction line from any crystalline substance was detected. The density of this glass was 3.9 g cm$^{-3}$.

2.2 Sample electrodes
The sample electrode was prepared to expose only one face of a thin glass plate to the electrolyte after connecting to a copper wire with silver paste on the gold-deposited back face. Epoxy resin was used for insulation. Strictly, the electrode surface was not a real plane but had a slight curvature.

2.3 Electrochemical measurements
A 1 mol dm$^{-3}$ LiClO$_4$ – propylene carbonate (PC) solution was used as the electrolyte. Both solvent and solute chemicals were dehydrated as usual. Using a potenti-galvanostat (input
impedance of the electrometer unit > 10\(^{12}\) \(\Omega\) and a data LOGGER (1 mV digit), the electrode potentials during and after intermittent galvanostatic reduction (−20 mA m\(^{-2}\), normally for 60 min) were measured against a lithium reference electrode. Another lithium electrode was employed as the counter electrode. All measurements were carried out at 25 °C under argon atmosphere.

3. RESULTS AND DISCUSSION

3.1 Electronic conductivity

The d.c. electrical conductivity, \(\sigma\), was determined from the slope of a current-voltage curve for a gold I glass slab I gold element, where the sample slab (ca. 0.4 mm thick) was prepared as in a previous work [1]. The obtained curve was linear over a wide range and no polarization phenomenon was observed.

The good linearity of a \(\ln \sigma T\) vs. \((1/T)\) plot as seen in Fig. 1 demonstrates that the small polaron hopping conduction is predominant [4], where \(T\) is the absolute temperature. The activation energy for conduction was 344 meV. The conductivity of 2.1\(\times10^{-7}\) S cm\(^{-1}\) at 296 K was lower by about one order than that (3.2\(\times10^{-6}\) S cm\(^{-1}\)) reported in the literature [2].

![Fig. 1 Temperature dependence of the d.c. conductivity](image)

3.2 Steady-state open-circuit potential of lithiated glasses

Curve 1 in Fig. 2 shows the steady-state open-circuit potential, \(U_{ss}\), of lithiated glasses. As well as in a case of single crystal \(V_2O_5\) [5], the value of \(U_{ss}\) was determined by the empirical method as explained in Fig. 3. The open-circuit recuperation potential, \(U_{oc}\), shifts linearly with the inverse square root of a recuperation time, \(t_{oc}\), as demonstrated by typical examples in Fig. 3. The values of \(U_{ss}\) were obtained by extrapolating these lines to \((t_{oc})^{-1/2} = 0\), that is, to the infinity of a recuperation time. The potential at the end of each recuperation period (23 h) was regarded as quasi-equilibrium, since its time derivative had diminished below 2 mV h\(^{-1}\). These finally observed potentials (Δ plots in Fig. 2) were more negative than \(U_{ss}\) typically by ca. 10 mV.

The concentration of lithium, \(x\), defined as a mean atomic ratio of (Li/V) was calculated from the weight of a sample glass and the integrated amount of charge passed through it. Though the coulombic efficiency for the electrochemical lithiation was assumed to be 100%, it should be confirmed experimentally in further studies.

Here, we replace \(U_{ss}\) with the equilibrium electrode potential, \(U_{eq}\), which is related to the activity of lithium in the glass phase, \(a_{Li}\). The slope of the coulometric titration curve at a certain point is expressed by the thermodynamic factor of lithium in the glass phase, \(K\), as follows.

\[
(dU_{eq} / dx) = (-RT / F)(K / x) \tag{1}
\]

where \(R\) and \(F\) are a gas constant and Faraday constant, respectively. The thermodynamic factor \(K\) defined by

\[
K = (\ln a_{Li} / \ln x) \tag{2}
\]

includes the non-ideality of a Li–glass solid solution [6] which originates from the interaction between inserted Li\(^+\) ions and from site limitations for Li\(^+\) ions and/or electrons.

**Curve 2 in Fig. 2** shows that the value of \(K\) calculated from eq.(1) increases with increasing \(x\). This tendency was common to all samples, though the absolute position of coulometric titration curves shifted from one to another electrode within a range of ca. 300 mV. In order to discuss the \(x\) dependence of \(K\), the position of inserted Li\(^+\) ions in the glass network should be made clear. Probably, they are located as distant to each other as possible to minimize the...
3.3 Galvanostatic lithiation potential

The time dependence of the galvanostatic lithiation potential, $U_{gs}$, can be described [3, 5, 8] by

$$\frac{dU_{gs}}{d\sqrt{t_{gs}}} = \frac{2RT}{F^2B}(K/x\sqrt{D})$$

(3)

under the following assumptions; (i) the only time-dependent overpotential is the concentration overpotential in the solid phase, and (ii) the diffusion of Li$^+$ ion to the interior of the solid phase can be treated as semi-infinite, where $t_{gs}$; galvanostatic lithiation time, $j$; current density, $D$; chemical diffusion coefficient of lithium, $B$; conversion factor from molar concentration to $x$.

Some examples for the $U_{gs}$ vs. $\sqrt{t_{gs}}$ plot were shown in Fig. 4. Straight lines seen in this figure show that eq.(3) holds within an initial lithiation period of ca. 100 s.

---

**Fig. 2** Typical coulometric titration curve (curve 1) and the calculated thermodynamic factor of lithium as a function of $x$ (curve 2)

- ○ : $U_{gs}$ as determined in Fig. 3
- Δ : finally observed recuperation potential

**Fig. 3** Typical transient potential changes as functions of the inverse square root of recuperation time in the GITT sequence ending at

1; $x = 4.9 \times 10^{-4}$
2; $x = 3.4 \times 10^{-3}$

interaction energy.

The cation insertion limit was not found out in a limited scope of the present study. When a higher current density of $\sim 200$ mA m$^{-2}$ was employed for the lithiation, the irreversible nucleation of an ionically conducting surface layer was observed and another type of the $U_{gs} - x$ relationship was obtained. This phenomenon was pointed out previously [1] and will be reported in a succeeding paper [7] in more detail.

**Fig. 4** Typical transient potential changes as functions of the square root of time in the GITT sequence starting from

1; $x = 2.0 \times 10^{-3}$
2; $x = 2.9 \times 10^{-3}$

sample A (20 μm thick), $- 20$ mA m$^{-2}$

As can be seen in Fig. 5, the slope of $U_{gs} - \sqrt{t_{gs}}$ line decreases with repeating the galvanostatic titration. The absolute values of $(dU_{gs}/d\sqrt{t_{gs}})$ for sample electrodes A and B are different to each other at $x \sim 4 \times 10^{-3}$, although they should be identical because the same lithiating current was applied. According to eq.(3), the decrease in $(dU_{gs}/d\sqrt{t_{gs}})$ corresponds to the increase in $D$, if the term of ($K/x$), or $(dU_{eq}/dx)$, is assumed to be constant. The data starting from $x = 0$ should be wasted because the unlihtiated glass can never show the reversible
potential for lithium insertion.

![Graph showing change in slope of a U_{gs} - \sqrt{I_{gs}} line in the GITT sequence](image)

Fig. 5 Change in the slope of a $U_{gs} - \sqrt{I_{gs}}$ line in the GITT sequence
- sample A (20 μm thick), $-20$ mA m$^{-2}$
- sample B (20 μm thick), $-20$ mA m$^{-2}$

3.4 Chemical diffusion coefficient of lithium and related quantities

Figure 6(A) shows typical datum for the chemical diffusion coefficient of lithium calculated by eq.(3). The magnitude of $D$ is virtually constant at $4\times10^{-12}$ cm$^2$s$^{-1}$. It is questionable whether the smaller values obtained at $x < 4\times10^{-3}$ originate from the experimental error of $K$-values or have a certain physicochemical meaning.

Figure 6(B), on the other hand, shows the component diffusion coefficient of Li$^+$ ion, $D_k$, which was calculated by the following equation

$$D_k = D / K \quad [4],$$

where the transport number of electrons is assumed to be unity [3]. The values of $D_k$ were also in the order of $10^{-12}$ cm$^2$s$^{-1}$, which correspond to a mobility of $1.6\times10^{-10}$ cm$^2$s$^{-1}$ V$^{-1}$ according to the Nernst-Einstein relation. Furthermore, the partial conductivity of Li$^+$ ion can be calculated as the product of this mobility and its concentration, which amounts to $4\times10^{-9}$ S cm$^{-1}$ at the last stage of this experiment ($x = 0.01$). The electronic conductivity of lithiated glasses will be higher than that of an original glass ($2.1\times10^{-7}$ S cm$^{-1}$ at 296 K), since +4 valent vanadium is increased by the lithiation.

![Graph showing changes in (A) the chemical diffusion coefficient of lithium and in (B) the component diffusion coefficient of Li$^+$ ion with $x$](image)

4. CONCLUSION

The mobility of Li$^+$ ion and its related quantities in a V$_2$O$_5$ – TeO$_2$ (50–50 mol%) glass were determined by using an electrochemical technique. The chemical diffusion coefficient of a Li$^+$ ion – electron pair was about $4\times10^{-12}$ cm$^2$s$^{-1}$ at 25 °C.

REFERENCES