

Inhomogeneous electrochemical lithiation of V_2O_5 - TeO_2 binary glasses in a propylene carbonate solution

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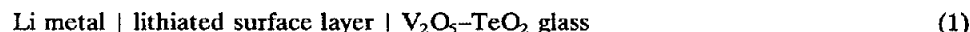
Abstract

The electronically-conducting V_2O_5 - TeO_2 binary glass thin plates were cathodized galvanostatically in an $LiClO_4$ /propylene carbonate solution at 25 °C. The lithiated glass surface was investigated by scanning electron microscopy (SEM) and it was revealed that lithium insertion takes place with a two-dimensional microscopic inhomogeneity on the glass surface. As well as the coulombic titration data, these observations suggested that a kind of phase-separation phenomenon was induced by electrochemical lithiation at an ambient temperature. Such a kind of structural change in a lithium host, of course, leads to the unfavorable degradation when applied to a secondary cell cathode.

Introduction

So far, various amorphous transition metal chalcogenides were examined as a cathode material for a lithium secondary cell as reviewed recently by Yamamoto [1]. Although some advantageous features of a glassy cathode material were claimed by Pagnier *et al.* [2], it is still questionable whether these amorphous materials behave as a solid-solution electrode during electrochemical insertion/extraction of Li.

The presence of unrechargeable Li was reported for discharge/charge cycled V_2O_5 - P_2O_5 glasses [3], which could be interpreted as a result of the phase separation phenomenon triggered by electrochemical lithiation. On the other hand, we have demonstrated clearly in a previous paper [4] that a lithium-ionically conducting phase is formed on the surface of an electronically-conducting 50 mol% V_2O_5 -50 mol% TeO_2 binary glass plate after electrochemical lithiation in an $LiClO_4$ /propylene carbonate (PC) solution, on a basis of the steady-state electromotive force (emf) measurements of a solid-state cell:



The evolution of a new phase seems likely especially in the metastable host matrix of a glass and, most probably, corresponds to the crystallization phenomenon of this binary glass after Li insertion. Furthermore, the X-ray diffraction (XRD) investigation of a chemically, *not electrochemically*, lithiated V_2O_5 - TeO_2 binary glass powder, revealed that a certain crystalline substance (not yet identified) is formed after LiI lithiation in a PC solution [5].

In a series of our studies on the electrochemical application of electronically-conducting V_2O_5 glasses [4, 6], this paper emphasizes that V_2O_5 - TeO_2 binary glasses do not behave as a solid-solution electrode for Li and that Li insertion takes place

inhomogeneously on the glass surface accompanied by the structural change of a glass host. Such a kind of degradation of a Li host, of course, is unfavorable for its application to a secondary cell cathode, since the appearance of the second phase in a host matrix should lower the reversibility of insertion/extraction cycles of Li.

Experimental

Preparation of glass samples

V₂O₅ (purity >99.5%) and TeO₂ (purity >99%) powders were melted in a platinum crucible at 800 °C for 40 min, where the melt was mixed up after every ~5 min to prevent the separation of the two components. Then the melt was quenched on a stainless-steel plate preheated at 170 °C. In contrast to amorphous pure V₂O₅ [7–9], a special rapid quenching technique is not necessary to supercool this binary melt of which Te:V ratio coincides with that of the obtained glass [10].

The glass ingots were annealed at 180 °C for 300 min. The sample glass had an a.c. conductivity of 2×10^{-7} S cm⁻¹ at 298 K and at 1 kHz. All the above procedures were carried out in an open air environment.

Electrochemical lithiation

A glass ingot was sliced by a diamond wheel cutter into several thin (~0.5 mm) slabs. Two segments facing to the atmosphere and to a quenching substrate were wasted because of the possible contamination. Then both upper and bottom faces of each slab were polished carefully with emery papers up to #4000 (Sumitomo 3M). Finally, the thin glass plate was mounted in a silicone resin to expose only one face after connecting with a copper wire through a vapor-deposited gold layer on the back face.

Electrochemical lithiation of a sample electrode was carried out galvanostatically by potentiogalvanostat (Toho Giken, Model 2020) in a commercially-available 1 M LiClO₄/PC solution (Mitsubishi Yuka) at 25 °C, where the electrode potential against a reversible Li electrode in the electrolyte was recorded continuously on a data logger (1 mV digit). Another Li electrode was employed as a counter electrode.

Analytical procedures

The electrochemically-lithiated sample electrodes were washed thoroughly with acetone several times. The XRD from a powdered sample or from the glass-plate surface was measured with a usual equipment using Cu K α radiation. Scanning electron microscopy (SEM) observation was carried out after evaporating a gold-palladium layer (~30 nm thick).

Results and discussion

Electrochemical aspects of lithiation reaction

The galvanostatic lithiation potential had a minimum point as seen in Fig. 1, which can be attributed to the diminishing nucleation overpotential of an Li-containing new phase in the glass matrix. Besides, the potential minimum could be found out on a coulombmetric titration curve in Fig. 2, where the finally observed recuperation potentials having a time dependence less than +1 mV h⁻¹ after each galvanostatic titration step were plotted against the (electron:vanadium) atomic ratio averaged over the entire volume a glass plate. The flame spectroscopic and the atomic absorption

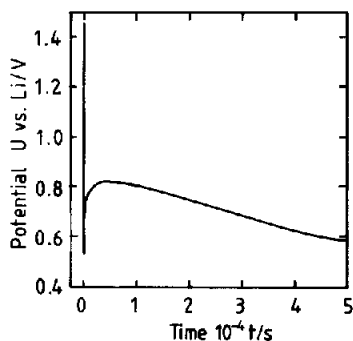


Fig. 1. Typical apparent lithiation potential of a 50mol%V₂O₅-50mol%TeO₂ electrode at $-20 \mu\text{A cm}^{-2}$ as a function of time, uncorrected for IR drop across a glass plate.

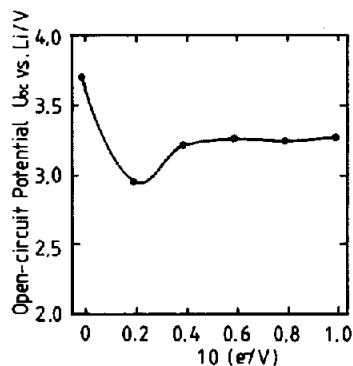


Fig. 2. A coulombmetric titration curve of a 50mol%V₂O₅-50mol%TeO₂ glass obtained from the sequential GITT (galvanostatic intermittent titration technique) measurements; each titration: $-20 \mu\text{A cm}^{-2} \times 28 \text{ h}$, and recuperation time $> 168 \text{ h}$.

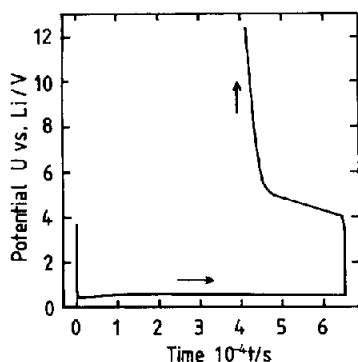


Fig. 3. The first galvanostatic discharge/charge cycle curves of a 50mol%V₂O₅-50mol%TeO₂ electrode at $\pm 10 \mu\text{A cm}^{-2}$.

analyses of Li in a glass sample ensured that the cathodic lithiation reaction proceeds almost quantitatively as a one-electron transfer reaction. Accordingly, the minimum point in Fig. 2 can be considered to correspond to the limit of supersaturation of Li in a glass matrix, which may also be regarded as the pseudo two-phase region of an intercalation electrode [11].

Furthermore, electrochemically-inserted Li cannot be extracted perfectly as recognized from the first galvanostatic discharge/charge cycle curves in Fig. 3. The imperfect anodic extraction of Li can also be demonstrated by the cyclic voltammetric investigation, which will be reported elsewhere in detail. These facts suggest that there happened a kind of irreversible change of the two-dimensional V-O-V network glass structure [12] during the first electrochemical lithiation procedure. The analogous irreversible structural change of crystallization in an amorphous electrode material was reported for electrochromic $\alpha\text{-WO}_3$ thin films after coloration/bleaching cycled in a PC solution [13].

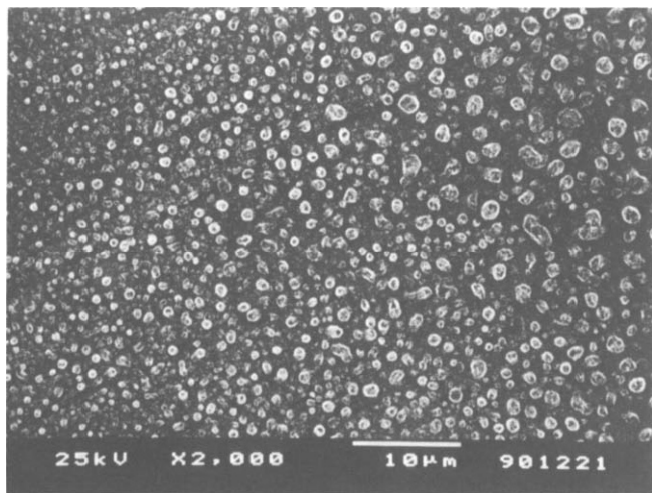


Fig. 4. The spot reaction sites on a 50mol%V₂O₅-50mol%TeO₂ glass surface observed by SEM; lithiation: $-20 \mu\text{A cm}^{-2} \times 13.9 \text{ h}$, and $(e^-:\text{V}) = 0.0050$.

Changes in the surface morphology after electrochemical lithiation

After electrochemical lithiation, we could observe, by SEM, on the glass surface many circular reaction spots as seen in Fig. 4. When electrochemical lithiation was continued for a longer time, even a cracked surface like a mosaic picture was observed. Unfortunately, the morphology of a lithiated glass surface is less reproducible at present and we can regard neither the amount of lithiation electricity nor a current density as a primary operation factor affecting the morphology of a lithiated surface.

No crystalline reaction product was detected by as-usual XRD investigation of the electrochemically-lithiated glass surface which had been suffered from an observable morphology change and accordingly from the replacement of constituent atoms in this binary glass. Hence, in contrast to the case of *chemical* LiI lithiation [5], it might be possible that the phase separation into two different amorphous phases, rather than the crystallization of an Li containing new phase, is responsible for the surface change induced by *electrochemical* lithiation. In fact, the locally separated nonuniform distribution of V and Te atoms could be confirmed by electron-probe microanalysis (EPMA) on the electrochemically-lithiated glass surface at $-20 \mu\text{A cm}^{-2}$.

Anyhow, such an electrochemically-induced structural change occurs within a limited depth and accordingly the (Li:V) ratio in this surface region should be extremely higher than that calculated on the basis of the uniform Li distribution in an entire glass slab. The same surface region formed by electrochemical lithiation in a PC solution has an Li⁺ ion conductivity, which was verified experimentally [4] by the measurements of steady-state emf and d.c. polarization of the above-mentioned solid-state cell (1).

Conclusions

50 mol%V₂O₅-50 mol%TeO₂ binary glass does not behave as a solid-solution electrode for Li in a PC solution. A further investigation is now continued for thermally

less stable glasses in this binary system (e.g., 85mol%V₂O₅–15mol%TeO₂), which presumably crystallize more easily by an externally applied perturbation.

Acknowledgement

The authors would like to thank Mr Isao San-nomiya for his experimental help for this study.

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