– Note –

Crystallization of V_2O_5 – TeO_2 Binary Glasses triggered by Chemical Lithiation with LiI in Propylene Carbonate

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1 INTRODUCTION

So far, some transition metal chalcogenides without any definite crystalline structure were examined as a positive pole material for a lithium secondary cell as reviewed recently by Yamamoto¹⁾.

We have demonstrated in a previous paper²⁾ that a lithium-ionically conducting phase is formed on the surface of an electronically conducting $50V_2O_5$ – $50TeO_2$ glass plate after electrochemical lithiation in an $LiClO_4$ –propylene carbonate (PC) solution, on a basis of measurements of a solid state cell

Li metal | lithiated surface | V_2O_5 – TeO_2 glass.

The occurrence of a new phase seems likely especially in the metastable matrix of a glass and, most probably, corresponds to the crystallization phenomenon of this glass triggered by lithium insertion. Such degradation of a lithium host, of course, is unfavorable for its application to a secondary cell, since the appearance of the second phase in a host matrix should lower the reversibility of insertion/extraction cycles of lithium.

In a series of our studies on the electrochemical application of electronically conducting V_2O_5 glasses^{2,3)}, this paper describes the crystallization of V_2O_5 – TeO_2 binary glasses observed after chemical lithiation instead of electrochemical one.

2 EXPERIMENTAL

2.1 Glass samples

As previously^{2,3)}, V_2O_5 (purity > 99%) and TeO_2 (purity > 99%) powders were melted in an alumina crucible at 850 °C for 45 min. Two molar compositions of $50V_2O_5$ – $50TeO_2$ and $67V_2O_5$ – $33TeO_2$ were chosen arbitrarily. The melt was quenched by dropping it into liquid nitrogen and then annealed at 170 °C for 180 min. The obtained glass droplets were crushed mechanically in an agate mortar and classified down to *ca.* 20 μm by a sedimentational procedure in acetone. Finally, a sample glass powder was dried in vacuum for 120 min.

These samples showed almost the same colour (orange yellow) as V_2O_5 and had an amorphous structure on a criteria of X-ray diffraction as shown

below. The average diameter of glass particles determined by a sedimentational method (Horiba, CAPA-500) in *n*-hexane was 5.2–5.3 μm .

2.2 Chemical insertion of lithium

A sample glass (*ca.* 0.3 g) was lithiated by 50 cm^3 of a 1 mol dm^{-3} LiI –PC solution at room temperature in a closed glass flask. During a reaction of

the 5 cm^3 aliquot of this solution was titrated by a standardized 0.01 mol dm^{-3} $Na_2S_2O_3$ aqueous solution⁴⁾ to determine a product of I_2 , where G represents a glass containing 1 mole of V_2O_5 . Before titration, both 5 cm^3 of acetone and 5 cm^3 of water were added to each aliquot.

Furthermore, a blank experiment was carried out in the absence of a glass powder to determine the amount of I_2 to be formed spontaneously in this system, and the amount of inserted lithium was calculated after correcting for these blank values. Though the following discussion is based on an inhomogeneous lithiation reaction localized at the surface region of a glass particle, the extent of lithiation is given conveniently as an atomic ratio of $(Li/V) = x$ averaged over the entire volume of a glass body.

Lithiated glass powders were washed with acetone and then dried in vacuum.

2.3 X-ray diffraction and SEM observation

X-ray diffraction from powdery samples was measured with a usual equipment using $CuK\alpha$ radiation. SEM observation was carried out after evaporating a gold–palladium layer (*ca.* 30 nm thick).

3 RESULTS AND DISCUSSION

3.1 Chemical lithiation reaction

In Fig. 1, the squared amount of lithiation, x^2 , is plotted against a reaction time, t . A linear relationship observed only at the initial stage suggests that the kinetics obeys a parabolic rate law for a diffusion-controlled reaction on a planar solid surface. However, it is difficult to estimate the diffusion coefficient of lithium in the glass phase, since its concentration in a surface layer is unknown at present.

The average flux of lithium, which is calculated as a lithiating current density from the slope of $x-t$ curves and the total surface area of a glass powder, decreases with a reaction time from 10^{-7} to 10^{-8} A cm^{-2} .

3.2 X-ray diffraction from crystalline product

Figure 2 compares typical X-ray diffractograms before and after chemical lithiation. It is undoubtful

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Fig. 1 Progress of chemical lithiation reaction obeying parabolic rate law

1: $50\text{V}_2\text{O}_5\text{--}50\text{TeO}_2$ 2: $67\text{V}_2\text{O}_5\text{--}33\text{TeO}_2$

Fig. 2 X-ray diffraction patterns of a glass powder

1: $50\text{V}_2\text{O}_5\text{--}50\text{TeO}_2$, original
2: $50\text{V}_2\text{O}_5\text{--}50\text{TeO}_2$, $x = 0.10$
3: $67\text{V}_2\text{O}_5\text{--}33\text{TeO}_2$, $x = 0.20$

that at least one crystalline substance is formed after lithiation by LiI. Furthermore, a set of diffraction angles from a lithiated sample is virtually independent of the composition of a mother glass.

It is difficult to assign all diffraction lines completely to any of following pure substances; LiI (JCPDS 1-0592), V_2O_5 (9-387), TeO_2 (paratellurite, 11-693), TeO_2 (tellurite, 9-433), $\alpha\text{-Li}_{0.04}\text{V}_2\text{O}_5$ (19-734), $\beta\text{-Li}_{0.30}\text{V}_2\text{O}_5$ (18-755), $\gamma\text{-LiV}_2\text{O}_5$ (18-756), $\text{Te}_2\text{V}_2\text{O}_5$ (18-1330) and LiVTeO_5 (26-1203). However, a set of the four strongest diffraction lines indicated on curves 2 and 3 may be attributed to $\alpha\text{-Li}_{0.04}\text{V}_2\text{O}_5$ (and hence to V_2O_5) supposingly, which implies the destruction of a vanadate network⁵⁾ forming a glass structure at >50 mol% of V_2O_5 .

3.3 Change in surface morphology

SEM views in Fig. 3 show that sharp broken edges of a original powder diminishes after lithiation and that many small plane scales like on a fish skin are

Fig. 3 Changes in surface morphology by chemical lithiation (bar = 5 μm)

(A): $67\text{V}_2\text{O}_5\text{--}33\text{TeO}_2$, original
(B): $67\text{V}_2\text{O}_5\text{--}33\text{TeO}_2$, $x = 0.20$

formed on the lithiated glass surface. X-ray diffraction lines should be ascribed to these plane crystallites.

4 CONCLUSIONS

At least one crystalline substance is formed on the $\text{V}_2\text{O}_5\text{--TeO}_2$ binary glass surface during chemical lithiation by LiI, though its lattice structure is not identified clearly at present. The same phenomenon seems to take place also during electrochemical lithiation as discussed in a previous paper²⁾, which may lower a coulombic efficiency for discharge/charge cyclings of these glasses in a lithium secondary cell.

It should be noted here that no crystalline substance was formed in preliminary experiments employing another reducing agent of *n*-butyllithium in *n*-hexane. This, at the same time, ensures that a kind of crystal is formed not by drying procedure but by LiI-lithiation itself.

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