

Time and Composition Dependent Electrical Conductivity of Vanadate Glasses Showing Both Cationic Conduction and Electronic Conduction*

Atsushi Ikeda, Ken-ichi Fukuda, and Tetsuaki Nishida**

Department of Biological and Environmental Chemistry, Kyushu School of Engineering, Kinki University
Kayanomori II-6, Iizuka 820-8555, Japan

RECEIVED JUNE 18, 2003; REVISED AUGUST 27, 2003; ACCEPTED SEPTEMBER 12, 2003

Key words
electrical conducting oxide glass
ionic conduction
electron hopping
polarization
silver vanadate glass
lithium vanadate glass

Silver vanadate glasses show electrical conductivity higher than 10^{-2} S cm $^{-1}$, caused by the electron hopping from V IV to V V together with an ionic conduction due to Ag $^+$. Lithium vanadate glasses show electrical conductivity of the order of 10^{-6} S cm $^{-1}$ which is primarily due to an electron hopping from V IV to V V . Fraction of the Ag $^+$ or Li $^+$ conduction and that of electron hopping from V IV to V V can be estimated by measuring both AC- and DC-conductivities. The latter becomes saturated after 50 min or more due to polarization of the mobile Ag $^+$ or Li $^+$ ions at around the cathode.

INTRODUCTION

Semiconductivity of vanadate (V₂O₅-based) glass is known to be caused by a step-by-step electron (*small polaron*) hopping from V IV to V V .¹⁻⁶ Mössbauer spectra of alkali or silver vanadate glasses proved that a structural change of skeleton structure takes place from the original two-dimensional layer structure of V₂O₅ (Ref. 7) to a pseudo-chain structure.¹⁻⁵ Mössbauer study of barium or magnesium vanadate glasses showed a structural change from a two-dimensional layer structure to a three-dimensional network structure.⁶ These results indicate that Mössbauer spectroscopy is very effective for characterizing electrical conducting glass since iron(III) occupies substitutional sites of Al III , B III , Si IV , V IV , etc.

Potassium iron(III) vanadate glass, 25K₂O · 65V₂O₅ · 10Fe₂O₃, showed a significant increase in the electrical conductivity from the order of 10^{-8} to the order of 10^{-4}

S cm $^{-1}$ after short-time heat treatment (isothermal annealing) at around the crystallization temperature (T_c).¹ Mössbauer spectra of heat-treated samples show a gradual decrease in quadrupole splitting and that in linewidth, indicating *structural relaxation* of the structural units like FeO₄, VO₄, and VO₅ that constitute a pseudo-chain structure.¹ More significant increase in the electrical conductivity could be achieved from the order of 10^{-7} to the order of 10^{-2} S cm $^{-1}$ when barium iron(III) vanadate glass was heat treated at around T_c , owing to a decrease in the distortion of the structural units which constituted three-dimensional network structure.⁸ The significant increase in the electrical conductivity can be ascribed to an increased probability of the *small polaron* hopping from V IV to V V caused by the *structural relaxation*. It is considered that lowering of 3d-orbital level of V V or V IV in less distorted VO₄ tetrahedra causes a decrease in the band gap between the valence band and the

* Dedicated to Professor Nenad Trinajstić on the occasion of his 65th birthday.

** Author to whom correspondence should be addressed. (E-mail: nishida@fuk.kindai.ac.jp)

conduction band, *i.e.*, a decrease in the activation energy for *small polaron hopping*.

This study was carried out in order to investigate the electrical conducting glasses that show both ionic conduction and electronic conduction. Fraction of the ionic conduction and that of the electronic conduction were estimated from the measurements of both DC- and AC-conductivities.

EXPERIMENTAL

Sample Preparation

A series of semiconducting silver vanadate glasses, $x\text{AgI} \cdot (75-x)\text{Ag}_2\text{O} \cdot 24\text{V}_2\text{O}_5 \cdot \text{Fe}_2\text{O}_3$, were prepared from AgI, Ag_2O , V_2O_5 , Fe_2O_3 of guaranteed reagent grade. Weighed amount of each reagent mixture was pulverized thoroughly in an agate mortar. A reagent mixture placed in a platinum crucible was melted in an open air in an electric muffle furnace at 900 °C for 15 min. Homogeneous glass samples of dark brown color were prepared by pouring the melt on a copper plate. A series of semiconducting lithium vanadate glasses, $x\text{LiI} \cdot (38-x)\text{Li}_2\text{O} \cdot 56\text{V}_2\text{O}_5 \cdot 6\text{Fe}_2\text{O}_3$, were prepared in a similar way from LiI, Li_2O , V_2O_5 , and Fe_2O_3 of guaranteed reagent grade. Each reagent mixture in a platinum crucible was melted at 1200 °C for 30 min in an open air in an electric muffle furnace. Homogeneous glass samples of dark brown color were prepared by partially immersing platinum crucible into ice-cold water.

Methods

DC four-probe and AC two-probe methods were used for the measurement of electrical conductivity of AgI- or LiI-containing vanadate glasses. Either edge of a rectangular glass sample was coated with silver paste. After the silver paste was dried for more than 1 h, four copper leads were attached to the silver paste with silver-containing solder. Electrical conductivity was determined by measuring the voltage of each sample under different values of DC-currents. AC two-probe method using an »AC-bridge« was used for determining the fraction of the ionic conduction in the total electrical conductivity of vanadate glasses in which ionic conduction and electron hopping are coexisting.

RESULTS AND DISCUSSION

AgI-containing Vanadate Glass

Time-dependent change of the electrical conductivity of $x\text{AgI} \cdot (75-x)\text{Ag}_2\text{O} \cdot 24\text{V}_2\text{O}_5 \cdot \text{Fe}_2\text{O}_3$ glasses, measured by four-probe DC method, are plotted in Figure 1. We can understand from Figure 1 that the electrical conductivity is higher at the initial stage of the measurements and decreases later. After 50 min measurement, it becomes saturated showing a conductivity of $6.3 \times 10^{-6} \text{ S cm}^{-1}$. The higher conductivity observed at the initial stage of measurements is ascribed to a remarkable migration of

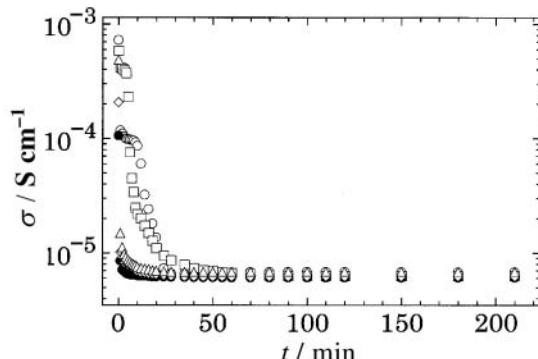


Figure 1. Time-dependent change of the electrical conductivity of $x\text{AgI} \cdot (75-x)\text{Ag}_2\text{O} \cdot 24\text{V}_2\text{O}_5 \cdot \text{Fe}_2\text{O}_3$ glasses; $x = 40$ (\circ), 45 (\triangle), 50 (\square), 55 (\diamond), 60 (\bullet).

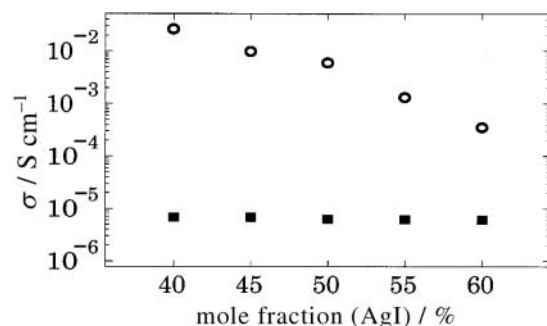


Figure 2. Total electrical conductivity (\circ) and the electrical conductivity by electron hopping after polarization (\blacksquare) in $x\text{AgI} \cdot (75-x)\text{Ag}_2\text{O} \cdot 24\text{V}_2\text{O}_5 \cdot \text{Fe}_2\text{O}_3$ glasses.

Ag^+ ions towards cathode. A marked decrease in the conductivity is observed within 30 min in Figure 1, indicating that most mobile Ag^+ ions have moved to the cathode and polarized there. Therefore, saturated electrical conductivity obtained after 50 min measurement can be related to the electron hopping from V^{IV} to V^{V} .

Composition dependency of the electrical conductivity can be understood from Figure 1. An increase in the AgI content (x) results in a decrease in the conductivity when the $(\text{V}_2\text{O}_5 + \text{Fe}_2\text{O}_3)$ content is fixed, as also illustrated in Figure 2. This is ascribed to a deviation of the $\text{AgI} / \text{Ag}_2\text{O}$ ratio from unity, since the $\text{AgI} / \text{Ag}_2\text{O}$ ratio of unity is the most favorable for the migration of Ag^+ ions. It is known that only the Ag^+ ions originating from AgI are essentially related to the ionic conduction.^{9–11} Such Ag^+ ions are surrounded by several I^- ions, constituting microdomains of AgI, which are located nearby the Ag_2O constituting the glass network.^{9–11} Microdomains of AgI are known to occupy interstices of the three-dimensional network of glass. In this study, Ag_2O , V_2O_5 , and Fe_2O_3 constitute a three-dimensional network structure.

Composition dependency of the electrical conductivity obtained from AC two- and DC-four probe methods is plotted in Figure 2. We can understand that the electrical conductivity marked with open circles, obtained by

the AC two-probe method, shows a gradual decrease with an increasing AgI content (x). Solid squares plotted in Figure 2 are »saturated« values of the electrical conductivity, *i.e.*, 6.3 to 6.8×10^{-6} S cm $^{-1}$, obtained by the DC four-probe method after 50 min measurement (see Figure 1). Since the values of the DC electrical conductivity saturated after 50 min measurement are primarily related to the electron hopping from V^{IV} to V^V, as described earlier, fraction (percentage) of the electrical conductivity due to electron hopping, $f(\text{elec})$, can be estimated from the following equation:

$$f(\text{elec}) = (\text{saturated DC conductivity} / \text{AC conductivity}) \times 100. \quad (1)$$

Hence, fraction of the ionic conductivity, $f(\text{ion})$, can be expressed by:

$$f(\text{ion}) = 100 - f(\text{elec}). \quad (2)$$

The $f(\text{ion})$ values obtained from Figure 2 are separately plotted in Figure 3. A slight decrease in the value of $f(\text{ion})$ is observed when AgI content (x) is 50 %, which is a critical value for one-dimensional chain structure. When the Ag₂O / (V₂O₅ + Fe₂O₃) ratio is unity, one-dimensional chain structure is formed, as reported earlier.^{1–5} In a one-dimensional chain structure, Ag⁺ will migrate easily in the interstices of the network.

When the AgI content (x) exceed 50 %, an Ag₂O / (V₂O₅ + Fe₂O₃) ratio becomes less than unity, indicating a gradual change of the network from one-dimensional chain to a two-dimensional layer. An inverse reaction was reported in AgI-containing silver vanadate glasses,^{3,4} in which an increase in the Ag₂O / (V₂O₅ + Fe₂O₃) ratio caused a change of the dimension of the network from two to one until the Ag₂O / (V₂O₅ + Fe₂O₃) ratio reached unity. Nishida and coworkers have reported that higher dimensional network shows higher electrical conductivity since the probability of electron hopping is increased when the dimension is high.^{4,8} It is noted that a slight decrease in the ionic conduction, $f(\text{ion})$, illustrated in Figure 3 is due to an increased degree of electron hopping from V^{IV} to V^V.

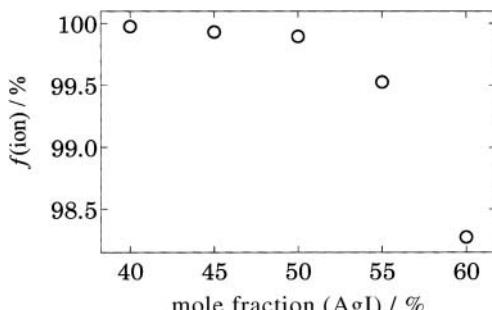


Figure 3. Fraction of the ionic conduction, $f(\text{ion})$, in $x\text{AgI} \cdot (75 - x)\text{Ag}_2\text{O} \cdot 24\text{V}_2\text{O}_5 \cdot 6\text{Fe}_2\text{O}_3$ glasses estimated from the results of Figure 2.

LiI-containing Vanadate Glass

Electrical conductivities of $x\text{LiI} \cdot (38 - x)\text{Li}_2\text{O} \cdot 56\text{V}_2\text{O}_5 \cdot 6\text{Fe}_2\text{O}_3$ glasses measured by four-probe DC method are plotted in Figure 4, which shows the electrical conductivity of the order of 10^{-6} S cm $^{-1}$. The electrical conductivity observed at the early stage of measurement is ascribed to a migration of Li⁺ ions. Figure 4 indicates that the conductivity slightly decreases after 120 min measurement and becomes saturated at the conductivity of about 5.2×10^{-6} S cm $^{-1}$. The slight decrease in the conductivity indicates that small number of mobile Li⁺ ions have moved to the cathode and hence the conductivity is primarily ascribed to the electron hopping from V^{IV} to V^V.

Figure 5 illustrates the electrical conductivity determined from AC two-probe (open circle) and DC-four probe method (solid squares). The former corresponds to the electrical conductivity associated with the Li⁺ conduction plus electron hopping, and the latter saturated conductivity primarily due to electron hopping from V^{IV} to V^V (see Figure 4). Fraction of the electrical conductivity due to the electron hopping, $f(\text{elec})$, in $x\text{LiI} \cdot (38 - x)\text{Li}_2\text{O} \cdot 56\text{V}_2\text{O}_5 \cdot 6\text{Fe}_2\text{O}_3$ glasses was estimated to be 3.0 to 6.5 %, as illustrated in Figure 6. Very small fraction of the ionic conduction is ascribed to small Li₂O / (V₂O₅ + Fe₂O₃) ratios ranging from 0.40 to 0.16 when the LiI contents (x) range from 13 to 28 %, respectively. The latter essentially

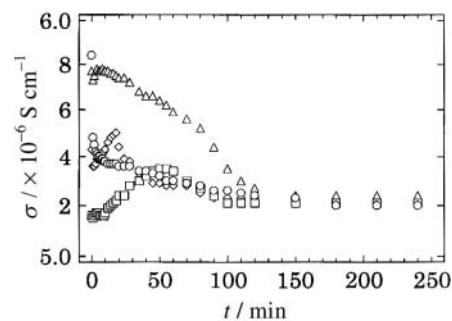


Figure 4. Time-dependent change of the electrical conductivity of $x\text{LiI} \cdot (38 - x)\text{Li}_2\text{O} \cdot 56\text{V}_2\text{O}_5 \cdot 6\text{Fe}_2\text{O}_3$ glasses; $x = 14$ (○), 19 (□), 24 (△), 29 (◇).

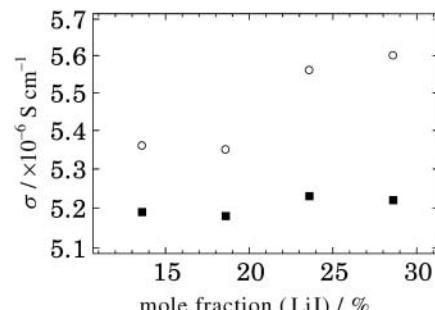


Figure 5. Total electrical conductivity (○) and the electrical conductivity by electron hopping after polarization (■) in $x\text{LiI} \cdot (38 - x)\text{Li}_2\text{O} \cdot 56\text{V}_2\text{O}_5 \cdot 6\text{Fe}_2\text{O}_3$ glasses.

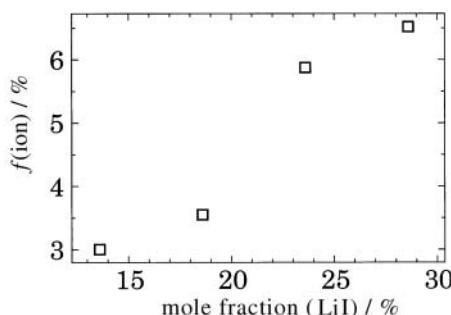


Figure 6. Fraction of the ionic conduction, $f(\text{ion})$, in $x\text{LiI} \cdot (38-x)\text{Li}_2\text{O} \cdot 56\text{V}_2\text{O}_5 \cdot 6\text{Fe}_2\text{O}_3$ glasses estimated from the results of Figure 5.

corresponds to two-dimensional layer structure similar to V_2O_5 .⁷ The former corresponds to an intermediate between two- and one-dimensional networks, as investigated in silver vanadate glasses.⁴ In vanadate glasses having a network structure of two- or three-dimension, the electron hopping from V^{IV} to V^{V} is predominant. In such a case, introduction of LiI will result in a small contribution of ionic conduction due to Li^+ .

CONCLUSIONS

Composition- and time-dependent behavior of the electrical conductivity is investigated in vanadate glasses containing Ag^+ or Li^+ . Combination of AC two-probe method and DC four-probe method makes it possible to easily determine the fraction of electrical conductivity due to ionic conduction and that due to electronic conduction, *i.e.*, an electron hopping from V^{IV} to V^{V} . Application of this method is not always restricted to vanadate glasses; it is useful for determining the electrical conductivity in which ionic conduction and electronic conduction are co-existing. Ionic conduction becomes predominant when the glass network has an open structure of lower dimension,

e.g., when $\text{Ag}_2\text{O} / (\text{V}_2\text{O}_5 + \text{Fe}_2\text{O}_3)$ ratio is close to unity, while the electronic conduction due to electron hopping becomes predominant when the glass has a network structure of higher dimension. This is the case for vanadate glass with a $\text{Li}_2\text{O} / (\text{V}_2\text{O}_5 + \text{Fe}_2\text{O}_3)$ ratio close to zero, since it has a two-dimensional layer structure. Also, higher degree of electron hopping will be predominant when the glass has a complicated three-dimensional network structure.^{4,8}

REFERENCES

1. T. Nishida, J. Kubota, Y. Maeda, F. Ichikawa, and T. Aomine, *J. Mater. Chem.* **6** (1996) 1889–1896.
2. T. Nishida, *Application of the Mössbauer Spectroscopy to the Chemistry*, in: F. E. Fujita (Ed.), *Introduction to the Mössbauer Spectroscopy – Principles and Applications*, Agne Gijutsu Center, Tokyo, 1999, pp. 169–266 [in Japanese].
3. T. Nishida, H. Ide, and Y. Takashima, *J. Ceram. Soc. Jpn.* **97** (1989) 284–288.
4. T. Nishida, H. Ide, Y. Takashima, T. Yagi, S. Tomariguchi, T. Ishizuka, and A. Sakai, *J. Mater. Sci.* **24** (1989) 1687–1692.
5. T. Nishida and Y. Takashima, *Bull. Chem. Soc. Jpn.* **60** (1987) 941–946.
6. T. Nishida, S. Saruwatari, and Y. Takashima, *Bull. Chem. Soc. Jpn.* **61** (1988) 2343–2346.
7. K. Jansen and G. Sperlich, *Phys. Status Solidi B*, **55** (1973) 495–502.
8. K. Fukuda, A. Ikeda, and T. Nishida, *Solid State Phenom.* **90–91** (2003) 215–220.
9. T. Minami, Y. Takura, and M. Tanaka, *J. Electrochem. Soc.* **124** (1977) 1659–1662.
10. T. Minami and M. Tanaka, *J. Non-Cryst. Solids* **38–39** (1980) 289–294.
11. T. Minami, K. Imazawa, and M. Tanaka, *J. Non-Cryst. Solids* **42** (1980) 469–476.

SAŽETAK

Električna vodljivost vanadatnih stakala, koja pokazuju kationsku i elektronsku vodljivost, u ovisnosti o vremenu i kemijskome sastavu

Atsushi Ikeda, Ken-ichi Fukuda i Tetsuaki Nishida

Ag-vanadatna stakla pokazuju električnu vodljivost veću od $10^{-2} \text{ S cm}^{-1}$ koja je prouzrokovana elektronskom promjenom oksidacijskog broja V^{IV} u V^{V} te doprinosom ionske vodljivosti Ag^+ . Li-vanadatna stakla pokazuju električnu vodljivost reda $10^{-6} \text{ S cm}^{-1}$ koja je prvenstveno prouzrokovana gubitkom jednoga elektrona iz iona V^{IV} ($\text{V}^{\text{IV}} - \text{e}^- \rightarrow \text{V}^{\text{V}}$). Udio iona Ag^+ ili Li^+ , odnosno elektronskoga doprinosa zbog oksidacije V^{IV} u V^{V} ukupnoj vodljivosti vanadatnih stakala može se procijeniti na temelju mjerena a.c.- i d.c.-vodljivosti. Nakon 50 minuta ili više, zbog polarizacije pokretnih iona Ag^+ ili Li^+ okolo katode, dolazi do katodnoga zasićenja te tehnika d.c.-vodljivosti nije više pouzdana.