

FAST ION-CONDUCTING GLASSES IN THE SYSTEM $\text{CuI-Cu}_2\text{O-V}_2\text{O}_5\text{-MoO}_3\text{-WO}_3$

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Glasses with unusually high ionic conductivity at a room temperature have been studied for many years by reason of their application in various electrochemical solid state devices such as rechargeable batteries and chemical sensors. New fast ion-conducting glasses were prepared in the basic system $\text{CuI-Cu}_2\text{O-MoO}_3$ by replacing MoO_3 with V_2O_5 and/or WO_3 . The glasses exhibited a high ionic conductivity at 25 °C in the range 0.22 to 0.87 S m^{-1} and much lower electronic conductivity, which was at least four orders of magnitude lower than the ionic conductivity. CuI positively affected the ionic conductivity, but decreased both glassforming ability and glass stability. The glassforming ability and stability of the glasses were improved by addition of V_2O_5 .

INTRODUCTION

Molten glasses usually exhibit good ionic conductivity, but in the solid state they are rather poor conductors. Even so, it was found that by using the rapid cooling techniques a special fast ion-conducting glass (FIC) could be prepared. These new materials have been studied for several years with the intention to use them as solid electrolytes for various electrochemical solid state devices such as rechargeable batteries and chemical sensors [1-3]. These glassy electrolytes have no grain boundaries that may cause problems for the transport of ions and their composition within a glass-forming region can be changed almost continuously.

One of the key characteristics of glassy electrolytes is sufficiently high ionic and low electronic conductivity at operating temperatures. This is necessary for the correct functioning of an electrolyte, e.g. in solid state batteries. To be a fast conductive, the FIC glass needs to contain enough highly mobile ions to carry the electric charge. The necessity for a high concentration of mobile ions (network modifiers) and for a loose structure to enable the easy movement of ions negatively impacts on the glass stability. Therefore, an optimum is to be sought by modifying the chemical composition of glass. The FIC glass-forming systems, which have been studied so far, comprise mainly of Li^+ , Na^+ , Cu^+ , and Ag^+ charge carriers and B_2O_3 , SiO_2 , P_2O_5 , V_2O_5 , and MoO_3 acting as network formers. The ionic conductivity at 25 °C, $\sigma_i(25)$, increases in the order $(\text{Na}^+) < (\text{Li}^+) < (\text{Cu}^+) \sim (\text{Ag}^+)$. Glasses containing only oxides can exhibit $\sigma_i(25)$ up to 10^{-5} S m^{-1} . Addition of halides, especially iodide, increases conductivity by several orders of magnitude. Halides probably form so-called "diffusion pathways" along which the cations can move easily [4]. However, very often a higher content of

halides destabilizes the glass network causing partial crystallization of the glass and consequently the decrease of its ionic conductivity.

The important role of tailoring the glass composition can be demonstrated by the following example. Common silica and boric glasses exhibit $\sigma_i(25)$ roughly from 10^{-17} to 10^{-9} S m^{-1} , but phosphate, molybdate, and vanadate FIC glasses containing CuI or AgI can reach $\sigma_i(25)$ in the range 10^{-2} to 10^0 S m^{-1} [4, 5].

Electronic conductivity of glass, because of its disordered structure, is usually very low, but the presence of the same elements in different oxidation states can promote this type of conductivity. This aspect should be taken into account when preparing FIC glasses in such systems. In most cases the electronic conductivity can be kept at least four orders of magnitude lower than the value of ionic conductivity.

EXPERIMENTAL PART

FIC glasses containing the Cu^+ ions were prepared in the following systems: $x\text{CuI} \cdot (50-x/2)\text{Cu}_2\text{O} \cdot (50-x/2) \cdot \text{MoO}_3$ and $44\text{CuI} \cdot 28\text{Cu}_2\text{O} \cdot y\text{V}_2\text{O}_5 \cdot z\text{WO}_3 \cdot (28-y-z) \text{MoO}_3$, where x was 25, 33.3, 38, and 44, y varied from 0 to 2 mol%, and z from 0 to 1 mol% (Table 1). The glasses were prepared from thoroughly mixed raw materials (CuI , MoO_3 , V_2O_5 , and WO_3) by melting the mixture in a silica glass tube at a dry argon atmosphere. The argon atmosphere was used to avoid oxidation of Cu^I and decomposition of CuI [6, 7]. Vitreous discs were made

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by quenching the melt in a steel forming mold. The prepared samples were examined using X-ray powder diffraction analyses (XRD) to determine if they contain crystals. For comparison XRD patterns of the polycrystalline samples that have the same composition as the glasses were also recorded. The crystalline samples were made by slow cooling of the melt.

Impedance spectroscopy was applied to determine the total conductivity (σ) of glasses. Glass discs with three sputtered Pt electrodes were used to assemble the electrochemical cell Pt|Cu⁺-glassy electrolyte|Pt. Impedance was measured in the frequency range 5 Hz to 500 kHz at 50 to 90 °C to determine the value of σ and its temperature dependence, which was used for the calculation of the total conductivity at 25 °C, $\sigma(25)$. To obtain the $\sigma(25)$, the σ values were fitted and extrapolated by the equation:

$$\sigma T = \sigma_0 e^{(-E_a/RT)} \quad (1)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy, T is the thermodynamic temperature, and R is the gas constant.

Ionic conductivity was calculated using the relation:

$$\sigma_i = \sigma - \sigma_e \quad (2)$$

where σ_i is the ionic and σ_e the electronic conductivity. The electronic contribution at 25 °C, $\sigma_e(25)$, to the $\sigma(25)$ was determined by means of Hebb-Wagner polarization technique using the cell (-)Cu|Cu⁺-glassy electrolyte|Pt(+), where Cu and Pt were the reversible and blocking electrodes, respectively [8].

To obtain the information on the structure of prepared materials, infrared spectra were recorded in the range 400 - 4000 cm⁻¹ using a Nicolet 740 FT-IR spectrometer. Additional information was acquired from differential thermal analyses (DTA) carried out at a heating rate of 10 °C min⁻¹ in the N₂ atmosphere. Chemical

durability was tested using distilled water. Bulk samples were immersed in hot water (80 °C) for 24 hours and the mass loss after the treatment was determined. Densities were measured at 20 °C using bulk samples free of bubbles. Xylene was used as a displacement liquid.

RESULTS

All prepared samples were amorphous except the sample containing 2 mol% of WO₃ which was partially crystalline. The prepared glasses were not hygroscopic and exhibited a good chemical durability in hot water. The dissolution of the samples in hot water was insignificant, because the mass losses were below 0.05% and no products of hydrolysis were observed on the glass surface.

The measured impedance data were analyzed using an equivalent circuit. As figure 1 shows, the circuit was made up of the resistance of leads (R_d) in series with inductance (L_d), the electrolyte bulk resistance (R_e), and the constant-phase element (CPE) representing the electrode-electrolyte interface. The σ values were calculated

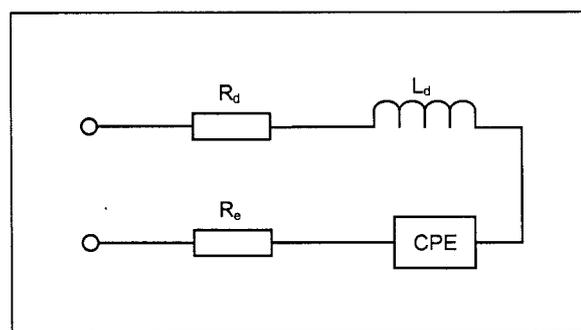


Figure 1. An equivalent circuit which models the behavior of the studied glassy electrolytes, R_e is the electrolyte bulk resistance, CPE is the constant-phase element, L_d is the inductance, and R_d is the resistance of leads.

Table 1. Glass compositions (mol%), total conductivity, $\sigma(25)$, pre-exponential factors, σ_0 , activation energies, E_a , and electronic conductivity, $\sigma_e(25)$.

ID	CuI	Cu ₂ O	V ₂ O ₅	WO ₃	MoO ₃	$\sigma(25)$ (S m ⁻¹)	$\sigma_0 \cdot 10^{-6}$ (S m ⁻¹ K)	E_a (kJ mol ⁻¹)	$\sigma_e(25) \cdot 10^6$ (S m ⁻¹)
A1	25.00	37.50	0.00	0.00	37.50	0.22	1.52	24.9	9.8
A2	33.33	33.33	0.00	0.00	33.33	0.55	1.83	23.1	7.0
A3	38.00	31.00	0.00	0.00	31.00	0.76	2.27	22.8	6.2
A4	44.00	28.00	0.00	0.00	28.00	0.87	3.33	23.4	7.9
B1	44.00	28.00	0.00	0.50	27.50	0.83	2.17	22.5	8.1
B2	44.00	28.00	0.00	1.00	27.00	0.57	4.60	25.3	7.3
C1	44.00	28.00	0.50	0.00	27.50	0.73	0.67	19.9	7.7
C2	44.00	28.00	1.00	0.00	27.00	0.65	2.72	23.7	7.9
C3	44.00	28.00	2.00	0.00	26.00	0.60	7.63	26.4	7.2
D1	44.00	28.00	0.33	0.33	27.34	0.83	2.36	22.7	11.2
D2	44.00	28.00	0.67	0.67	26.66	0.78	7.33	25.7	10.3
D3	44.00	28.00	1.00	1.00	26.00	0.63	2.54	23.6	9.9

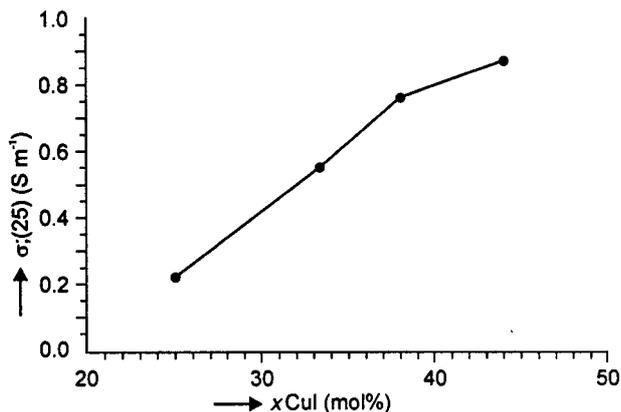


Figure 2. The effect of CuI on the ionic conductivity of glasses $x\text{CuI}\cdot(50-x/2)\text{Cu}_2\text{O}\cdot(50-x/2)\text{MoO}_3$ at 25 °C (table 1).

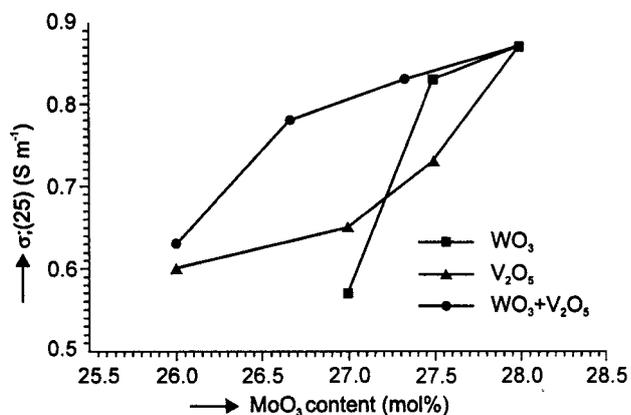


Figure 3. The effect of the partial substitution of V_2O_5 and/or WO_3 for MoO_3 on the ionic conductivity of glasses $44\text{CuI}\cdot 28\text{Cu}_2\text{O}\cdot y\text{V}_2\text{O}_5\cdot z\text{WO}_3\cdot(28-y-z)\text{MoO}_3$ at 25 °C. The legend indicates the component which is added at the expense of MoO_3 (table 1).

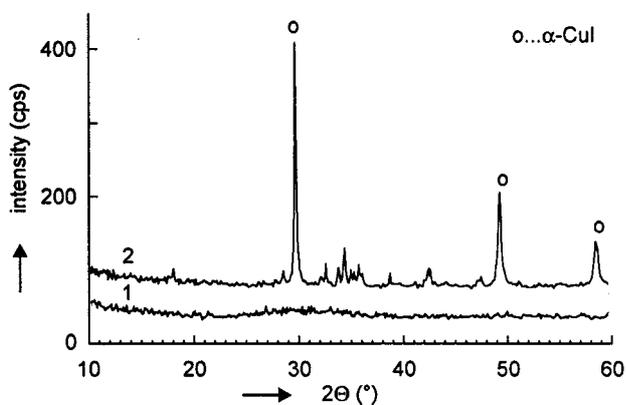


Figure 4. XRD patterns of the glass (1) and polycrystalline material (2) of the identical composition $44\text{CuI}\cdot 28\text{Cu}_2\text{O}\cdot 28\text{MoO}_3$.

ed from R_e and $\sigma(25)$ was estimated using equation (1). Table 1 shows the $\sigma(25)$ values, which were dependent on glass composition and span from 0.22 to 0.87 S m⁻¹. The $\sigma_e(25)$ values (table 1) were at least 4 orders of magnitude lower than $\sigma(25)$, which means that the electronic contribution to the total conductivity is negligible and the electric current is carried mostly by ions.

The favorable effect of CuI on the ionic conductivity at 25 °C, $\sigma_i(25)$, is illustrated in figure 2 and changes of $\sigma_i(25)$ when replacing MoO_3 with V_2O_5 and/or WO_3 are presented in figure 3. The glasses with a high content of CuI had lower glass forming ability, therefore, it was impossible to prepare vitreous materials containing more CuI than 44 mol% in the system $\text{CuI-Cu}_2\text{O-MoO}_3$. The additions of CuI resulted in the decrease of the E_a values except the glass with the highest CuI content (table 1).

Figure 4 compares XRD patterns of the glass and polycrystalline material of the identical composition $44\text{CuI}\cdot 28\text{Cu}_2\text{O}\cdot 28\text{MoO}_3$. Two crystalline phases cubic $\alpha\text{-CuI}$ and monoclinic $\text{Cu}_6\text{Mo}_5\text{O}_{18}$ were identified in the polycrystalline sample. The structure of $\text{Cu}_6\text{Mo}_5\text{O}_{18}$ is built with the octahedral MoO_6 units that share common edges. These units form four-membered groups, which are joined by other MoO_6 units as is shown in figure 5.

The prepared glasses exhibited IR absorption in the range 400 – 930 cm⁻¹ that is characteristic for molybdate groups [9]. The typical IR spectrum of these glasses together with the spectrum of polycrystalline $\text{Cu}_6\text{Mo}_5\text{O}_{18}$ is shown in figure 6. IR spectra of the glasses without V_2O_5 were very similar to that of $\text{Cu}_6\text{Mo}_5\text{O}_{18}$ denoting that the glasses possibly contain similar arrangement of the MoO_6 octahedral units as in $\text{Cu}_6\text{Mo}_5\text{O}_{18}$. The additions of V_2O_5 and/or WO_3 at the expense of MoO_3 slightly shifted the absorption maximum and changed width of the absorption band, which indicates structure modification [5].

Using DTA, the glass transition temperatures t_g (113 to 127 °C), the crystallization temperatures (141 to 358 °C), and the melting temperatures of crystalline phases (372 to 492 °C) were determined. The lowest t_g had the glass containing 44 mol% CuI without V_2O_5 . Replacing MoO_3 with V_2O_5 resulted in a t_g increase by 9 to 14 °C, on the other hand, replacing MoO_3 with WO_3 had no significant effect on t_g .

Densities of the glasses were from 5253 to 5362 kg m⁻³. While the additions of CuI or WO_3 increased the density, the additions of V_2O_5 decreased the density.

DISCUSSION

Some suggestions were made on the possible influence of chemical composition on the structure and conductivity of the prepared glassy electrolytes.

It is supposed that the most mobile ions in the prepared glasses are the Cu^+ cations [11, 12]. It is probable because the material is in a solid state and the Cu^+ cations are monovalent and have a small ionic radius

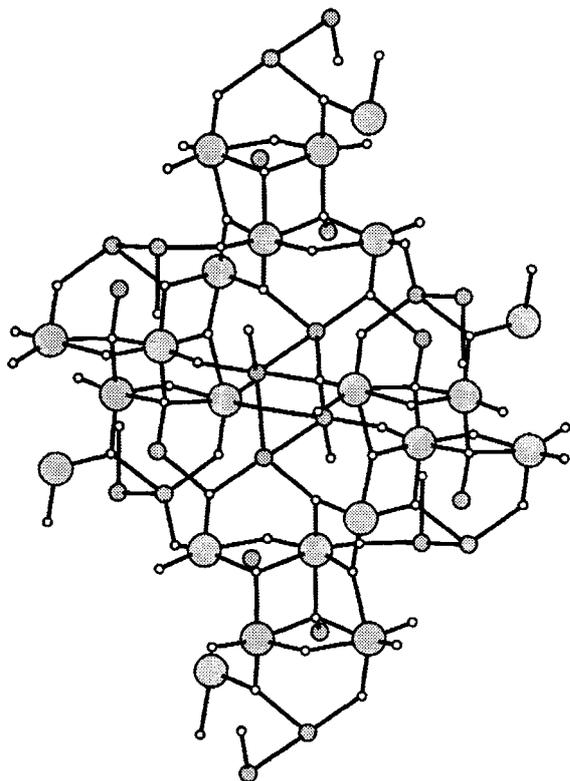


Figure 5. The model of the structure of $\text{Cu}_6\text{Mo}_5\text{O}_{18}$ [10].

● - Mo
● - Cu
○ - O

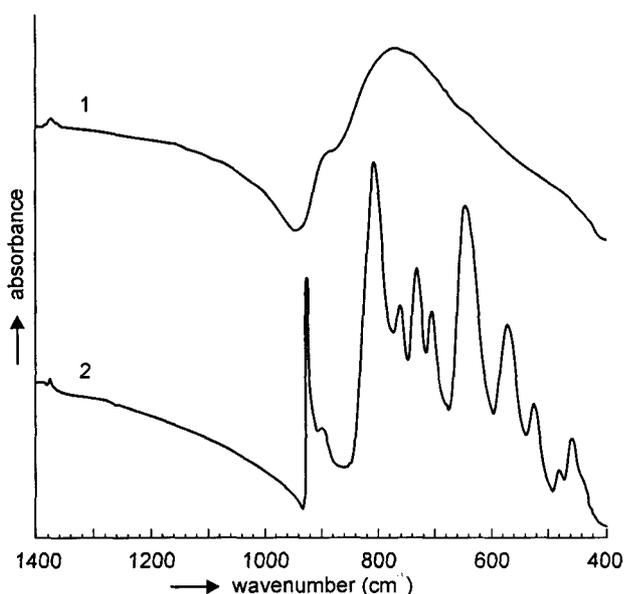


Figure 6. IR spectra of the glass 44CuI-28Cu₂O-28MoO₃ (1) and crystalline material $\text{Cu}_6\text{Mo}_5\text{O}_{18}$ (2).

($r = 96$ pm). The I⁻ anions ($r = 220$ pm) are much bigger and the O²⁻ anions ($r = 135$ pm) are divalent, therefore,

their mobility should be much lower [13, 14]. Thus, the electric charge is probably carried mostly by the Cu⁺ cations.

The positive effect of CuI on the ionic conductivity corresponds with the conception of the "diffusion path" model [4]. According to this model, bonds between Cu and I are weaker than that between Cu and O and thus the most mobile ions are the Cu⁺ ions bonded to the I⁻ anions which form so-called "diffusion pathways" for the Cu⁺ cations. IR measurements (figure 6) indicated the possibility that the prepared glasses could contain a similar type of structure as $\text{Cu}_6\text{Mo}_5\text{O}_{18}$. As figure 5 shows, MoO₆ units in $\text{Cu}_6\text{Mo}_5\text{O}_{18}$ are sharing edges, so that the structure of $\text{Cu}_6\text{Mo}_5\text{O}_{18}$ is quite closely packed. Therefore, the transport of ions through this type of structure might be difficult. These could be the reasons why CuI, which was added at the expense of Cu₂O and MoO₃, decreased E_a and positively affected $\sigma_i(25)$ although the total content of Cu⁺ was decreasing. However, CuI decreases glassforming ability and glasses with the CuI content close to the upper limit (44 mol%) have probably a weaker structure (t_g goes down to 113 °C) that can not prevent the higher ordering and closer packing of the I⁻ anions in the "pathways". This could cause that the increase of $\sigma_i(25)$ was not so steep within the high CuI region (figure 2) and E_a was slightly increasing (table 1).

Figure 3 shows that replacing MoO₃ with V₂O₅ and/or WO₃ affected $\sigma_i(25)$. It is possible that the composition changes result in structure modifications and consequently influence the ionic conductivity. The low content of WO₃ (to 0.5 mol%) had no significant effect, but the higher content (1 mol%) decreased the $\sigma_i(25)$. The octahedral WO₆ units exhibit a higher repulsion force than the MoO₆ units, therefore, they prefer to share corners instead of edges [15]. The substitution of the WO₆ units for the edge sharing MoO₆ units could loosen the glass structure and thus enable ordering and precipitation of α -CuI leading to the lower $\sigma_i(25)$ values. Addition of V₂O₅ probably strengthens the glass structure (t_g goes up from 113 to 127 °C), which could cause the decrease of $\sigma_i(25)$ because it will be more difficult for ions to get through this structure. In glasses with V₂O₅ the ratio Cu / (Mo + W + V) is lower than in the other glasses, because one Mo^{VI} atom was replaced by two V^V atoms. This probably leads to the more condensed structure obstructing the transport of ions. In glasses containing both WO₃ and V₂O₅ the effect of V₂O₅ is probably partially compensated by the effect of WO₃ and thus the decrease of $\sigma_i(25)$ is not so steep at the beginning.

CONCLUSIONS

It is possible to prepare the Cu⁺ fast ion-conducting glasses in the system CuI-Cu₂O-MoO₃ that exhibit the ionic conductivity at 25 °C up to 0.87 S m⁻¹ and very low electronic conductivity. Very favorable effect on the ionic conductivity has CuI. Properties of these glasses can be modified by replacing MoO₃ with

V_2O_5 and/or WO_3 . These glasses are new promising materials for the construction of solid state batteries, electrochemical sensors, and other solid state micro devices.

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SKLA S VYSOKOU IONTOVOU VODIVOSTÍ V SOUSTAVĚ $\text{CuI-Cu}_2\text{O-V}_2\text{O}_5\text{-MoO}_3\text{-WO}_3$

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Skla s vysokou iontovou vodivostí při pokojové teplotě jsou studována řadu let pro jejich použití v různých elektrochemických zařízeních, jako jsou například baterie a chemické senzory. V soustavě $\text{CuI-Cu}_2\text{O-MoO}_3$ se podařilo připravit nová skla s vysokou iontovou vodivostí nahrazováním oxidu MoO_3 oxidy V_2O_5 nebo WO_3 . Tato skla dosahují iontové vodivosti při 25°C od 0,22 do 0,87 S/m a současně nízké elektronové vodivosti, která je nejméně o čtyři řády nižší než vodivost iontová. CuI příznivě ovlivňuje iontovou vodivost, avšak snižuje sklotvornost a stabilitu skla. Sklotvornost a stabilita byly zlepšeny malým přídatkem V_2O_5 .