# Influence of Metal–Glass Contact on the Dynamic Response of $0.40Ag_2O: 0.60P_2O_5$ Glass

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#### Abstract

The results of impedance measurements on a low-conducting  $0.40 \text{Ag}_2 \text{O}: 0.60 \text{P}_2 \text{O}_5$  glass are reported in the frequency range  $10^{-3}$  to  $10^5$  Hz and the temperature range 250 to 400 K. The observed dispersions in the complex impedance data are attributed to a barrier effect in the region of the electrodes and are shown to follow simple power law behaviour for low and high frequencies with respect to the loss peak frequency. Using the complex impedance and complex capacitance data, the contact resistance and the corresponding contact capacitance have been worked out. The temperature dependences of the contact resistance  $R_s$  and the contact capacitance  $C_s$  are also reported. The activation energy for this glass is found to be  $0.50\pm0.02 \text{ eV}$ .

## 1. Introduction

Silver ion conducting glasses have been extensively studied recently as solid electrolytes, which are essential materials for electrochemical cells and related ion conducting devices (see for example Corette *et al.* 1983; Martin and Angell 1984; Magistris *et al.* 1983; Haque *et al.* 1993, 1994). Electrical measurements on glassy solid electrolytes are usually carried out by forming a simple cell on a pellet with two appropriate metal layers coated on opposite faces of the material under study; this often produces a Schottky-like barrier layer in the region of the electrodes (Hill and Pickup 1983). There has been a continuing interest in the study of the effects of electrode contacts on ionic conductors over many years. The exact nature of the metal–glass contacts and the effect of charge pile-up and non-perfect charge exchange at the electrodes are, as yet, imperfectly understood (Hill and Pickup 1983). The impedance response of a material with its electrodes measured over a wide range of frequencies can provide an excellent tool for the analysis of the data in terms of bulk and barrier regions, as the Cole–Cole impedance response clearly distinguishes these two regions.

Recent advances in the field of impedance measurements have suggested that solid electrolytes are dispersive in nature as most of the ionic conductors exhibit an inclined circular arc impedance diagram. The frequency dependence of the electrical impedance and capacitance of the majority of ionic conductors have largely been explained as being consequences of the distribution of relaxation times (Barker *et al.* 1976). Jonsher (1983) has suggested that the dispersion is a universal property of dielectric materials whereas Nagai and White (1979) and Dissado and Hill (1979) have proposed that dispersion is due to many-body interaction of the conducting species in the bulk of the materials. The strong dispersion observed in silver phosphate and silver borophosphate glasses has been interpreted as capacitive contributions from  $BPO_4$  and  $PO_4$  groups in the bulk along with an interfacial layer capacitance (Haque *et al.* 1994).

Many investigators (Bauerle 1969; Beekmans and Heyne 1976) have reported impedance spectroscopy and electrical resistance measurements of a wide range of materials. There appears to have been no detailed study of the low-frequency impedance in silver phosphate glasses. In our earlier work (Haque *et al.* 1993), a study of the a.c. conductance and tangent loss in silver phosphate and silver borophosphate glasses has been reported.

In the present paper we report a systematic study of the complex impedance  $Z(\omega)$  of a  $0.40 \text{Ag}_2 \text{O}: 0.60 \text{P}_2 \text{O}_5$  glass as a function of frequency  $(10^{-3}-10^5 \text{ Hz})$  over a wide range of temperatures (250–400 K). The glass composition selected for the present study is one of the lowest-conducting glasses in the family of silver phosphate glasses. Using the complex impedance data, the contact resistance and the corresponding contact capacitance have been worked out. Simple empirical power-law behaviour is proposed to relate the frequency dependence of the complex impedance data for the  $0.40 \text{Ag}_2 \text{O}: 0.60 \text{P}_2 \text{O}_5$  glass.

#### 2. Theory

When an electrical signal

$$U = U_0 e^{i\omega t} \tag{1}$$

is applied between the electrodes of a cell and the resulting current passing through the cell

$$I = I_0 e^{i\omega t + \phi} \tag{2}$$

is measured, the impedance of the cell can be written as

$$Z = U/I = U_0 e^{-i\phi}/I_0 = Z_0 e^{-i\phi}$$
$$= Z_0(\cos\phi - i\sin\phi)$$
$$= Z' + iZ''$$
(3)

where Z' is the real part and Z'' the imaginary part of the impedance Z. The simplest equivalent circuit diagram of a solid electrolyte on which electrodes have been superposed on its opposite faces is shown by a series combination of a bulk and a barrier region (see Fig. 1*a*). The bulk of the sample is represented by a finite d.c. conductance  $G_{\rm b} = 1/R_{\rm b}$  in parallel with the bulk capacitance  $C_{\rm b}$ , and the barrier region is represented by an equivalent barrier layer capacitance  $C_{\rm s}$ in series with an equivalent resistance  $R_{\rm s}$ . As the bulk and interfacial regions are electrically in series, the total impedance of the sample can be written as

$$Z = Z_{\rm b} + Z_{\rm s} \,, \tag{4}$$

where  $Z_{\rm b}$  is the impedance of the bulk and  $Z_{\rm s}$  the impedance of the interfacial region.

For the analysis of the impedance data in terms of the complex impedance plane, log f versus log  $Z(\omega)$  and  $Z'(\omega)$  versus  $Z''(\omega)$  are plotted. The general behaviour of these plots is shown in Figs 1b and 1c. In Fig. 1b,  $Z''(\omega)$  shows a peak and the  $Z'(\omega)$  curve exhibits a plateau, and this saturated value of  $Z'(\omega)$  may correspond to the total real impedance of the sample. Fig. 1c gives the Cole–Cole plot, in which  $Z'(\omega)$ , when plotted against the corresponding  $Z''(\omega)$ , gives rise to a semicircular arc. The diameter of this arc gives the bulk resistance. Figs 1b and 1c provide a straightforward determination of the electrolyte's resistance  $R_{\rm b}$ , the total real impedance of the sample, Z' = R and the contact resistance  $R_{\rm s} = R - R_{\rm b}$ . If the loss peak frequency  $\omega_{\rm p}$  corresponding to  $Z''_{\rm max}$  in Fig. 1c is known, the bulk capacitance  $C_{\rm b}$  can be determined using the relation  $1/\omega_{\rm p} = R_{\rm b}C_{\rm b}$ . The contact capacitance  $C_{\rm s}$  can be determined using the values of  $C_{\rm b}$ ,  $G_{\rm b}$  and the experimentally observed value of the real capacitance  $C'(\omega)$ .



Fig. 1. Equivalent circuit with an expected complex impedance: (a) equivalent circuit of the suggested conduction model; (b) frequency-dependent complex impedance response; and (c) Cole–Cole response of the complex impedance.

#### 3. Experimental Procedure

Reagent grade  $AgNO_3$  (JMC) and  $P_2O_5$  (Merck) were used to prepare the glass with composition  $0.40Ag_2O: 0.60P_2O_5$ , glass  $G_0$ , by a conventional



Fig. 2. Complex impedance plots for  $0.40 \text{Ag}_2\text{O}: 0.60 \text{P}_2\text{O}_5$  glass at different temperatures.



Fig. 3. Logarithmic plots of the complex impedance for  $0.40 \text{Ag}_2\text{O}: 0.60 \text{P}_2\text{O}_5$  glass at different temperatures.

quenching technique. X-ray diffraction analysis and glass transition temperature  $(T_{\rm g})$  studies confirmed the amorphous nature of this glass. For electrical measurements, gold electrodes of area  $0.58 \,{\rm cm}^2$  were deposited on both sides of the pellet, under a vacuum better than  $10^{-5}$  Torr  $(1 \,{\rm Torr} \equiv 133 \,{\rm Pa})$ . The instruments used for the dielectric measurements included a Solatron 1255 frequency response analyser (FRA) coupled with a Chelsea Dielectric Interface in conjunction with a PC (Opus-V), Roland DXY-880 plotter and Oxford DN1704 Cryostat with temperature controller ITC4. The experimental set-up used was the same as reported in an earlier study (Anis *et al.* 1992).

## 4. Results and Discussion

The principal feature of our experimental results is the presence of a strong dispersion in the complex impedance data, which we attribute to a barrier effect in the region of the electrodes. Fig. 2 shows the impedance plots,  $Z'(\omega)$  versus  $Z''(\omega)$ , for glass G<sub>0</sub>. The impedance plot for each temperature is displaced vertically for clarity. The inclined circular arcs of this figure clearly demonstrate the temperature dependence of the angle of depression  $\theta$  with the real axis. The angle of depression  $\theta$  of the semicircular arc is related to the power law exponent n by  $\theta = (1-n)\pi/2$ , and reflects the magnitude of the dispersion (Jonscher 1983). Fig. 2 exhibits a decrease in  $\theta$  with the increase in temperature, and may be interpreted as the imperfect charge conduction process at lower temperatures changing to a pure d.c. process at 400 K. All the depressed semicircular arcs at different temperatures correspond to the bulk impedances, and the tilted spikes intersecting the real axis at low frequencies correspond to some interfacial region. As can be seen, with an increase in temperature the depressed semicircular arcs are shifted towards higher frequencies with a decrease in their diameters, resulting in a smaller intercept on the real axis. These depressed semicircular arcs arise from the ionic migration in the bulk of the glassy electrolyte (Martin and Angell 1984). The frequency corresponding to  $Z''(\omega)_{\text{max}}$  is used to determine the bulk capacitance; the results are shown in Table 1. Fig. 3 shows typical  $\log Z(\omega)$ versus  $\log f$  plots for glass  $G_0$  measured at different temperatures. These plots exhibit low-frequency plateaus corresponding to the total real impedance of the sample under investigation. The results for bulk and interfacial impedances are given in Table 1. The contact resistance is found to be approximately 5 to 16% of the total sample resistance.

Table 1. Various dielectric parameters and their temperature dependences for a  $0.40 Ag_2 O: 0.60 P_2 O_5$  glass

T(K)	$\log(R_{ m b}/\Omega)$	$\log(R_{ m s}/\Omega)$	$\log(C_{\rm b}/{ m F})$	$\log(C_{\rm s}/{\rm F})$	Slopes		
					p	m	x
400	$5 \cdot 08$	3.77	-10.37	-1.78	0.78	0.73	1.64
375	$5 \cdot 49$	$4 \cdot 00$	-10.36	$-2 \cdot 35$	0.75	0.72	1.68
350	$5 \cdot 94$	$5 \cdot 11$	$-10 \cdot 31$	$-2 \cdot 75$	0.86	0.51	1.64
325	$6 \cdot 44$	$5 \cdot 26$	$-10 \cdot 24$	-3.65	$0 \cdot 92$	0.48	1.68
304	$6 \cdot 98$	$5 \cdot 60$	$-10 \cdot 27$	$-4 \cdot 16$	0.98	$0 \cdot 42$	1.88
275	$7 \cdot 53$	$6 \cdot 76$	$-10 \cdot 23$	-4.78	0.98	0.50	1.76
250	$8 \cdot 06$	$7 \cdot 03$	$-10 \cdot 11$	$-5 \cdot 45$	$0 \cdot 98$	$0 \cdot 48$	$1 \cdot 86$



**Fig. 4.** Variation of contact resistance  $R_s$  and contact capacitance  $C_s$  for  $0.40 \text{Ag}_2\text{O}: 0.60 \text{P}_2\text{O}_5$  glass at different temperatures.



**Fig. 5.** Arrhenius plot of  $\log f_p$  against 1/T.

The temperature dependences of the contact resistance and the contact capacitance for this glass are shown in Fig. 4. A decrease in contact resistance and an increase in contact capacitance with an increase in temperature can be seen in this plot, clearly indicating the formation of the space charge region in the vicinity of the electrodes as more charge accumulates at the interface with the increase in temperature, which reduces the width of the interface and hence reduces its resistance and increases its capacitance.

In view of the power law behaviour, impedance data of different slopes as a function of temperature are given in Table 1. The high- and low-frequency data follow simple power law trends as  $Z'' \propto \omega^{-p}$  and  $Z' \propto \omega^{-x}$  for high frequencies, and the low-frequency data follow  $Z'' \propto \omega^{-m}$  and  $Z' \propto \omega^0$ , where p is the high-frequency slope of Z'', x is the high-frequency slope of Z'', and m is the low-frequency slope of Z'' measured from the log-log plots. A plot of  $\log f_p$  versus 1/T, where  $f_p$  is the loss peak frequency calculated from impedance plots, is shown in Fig. 5, which exhibits Arrhenius behaviour. The value of the activation energy calculated from this plot is  $0.50\pm0.02$  eV.

## 5. Conclusions

An electrode–electrolyte interface exerts an influence on  $Z(\omega)$  measurements carried out on  $0.40 \text{Ag}_2 \text{O}: 0.60 \text{P}_2 \text{O}_5$  glass. The contact resistance is found to be 5 to 16% of the total resistance of the sample, and the contact capacitance ranges from  $1 \times 10^{-6}$  to  $1 \times 10^{-2}$  F. A decrease in contact resistance and an increase in capacitance with increasing temperature of the glassy sample indicate the development of a space charge region in the vicinity of the electrodes. The overall complex impedance response exhibits power law behaviour. The value of the activation energy is found to be  $0.50\pm0.02$  eV.

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Manuscript received 7 February, accepted 29 April 1994