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Electrochemical investigation on the contact in solid state cells with an $RbAg_4I_5$ electrolyte

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The contact between a silver electrode and the solid electrolyte $RbAg_4I_5$ is investigated by means of impedance and cyclic voltammetry. From the observed dependence of the electrolyte resistance and the maximum current density achievable in cyclic voltammetry on the pressure applied, an attempt is made to calculate the real contact areas.

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1. Introduction

Since the first reports on the fast solid ionic conductor $RbAg_4I_5$ [1, 2], much work has been done on this compound [3]. Electrochemical investigations have been made particularly by Armstrong *et al.* [4–10] but also by other workers [11, 12]. Nevertheless, the information obtainable on the interphase and contact between a solid electrolyte and a solid electrode is still incomplete. Because of its exceptionally high conductivity at room temperature, $RbAg_4I_5$ was chosen as a model electrolyte to investigate some properties of the solid–solid interphase. Cyclic voltammetry and impedance measurements were applied to seek the desired information.

2. Experimental

The solid electrolyte $RbAg_4I_5$ was prepared from a 4 : 1 mixture of AgI and RbI by melting this mixture in an alumina crucible and quenching the melt to room temperature. The solidified melt was then ground and annealed for about 15 h at 160° C.

For cyclic voltammetry a three-electrode cell consisting essentially of a teflon cylinder within a steel housing, described elsewhere [13] was employed (cell I). A Ag/AgI-wire was used as the reference electrode.

For measurements under pressure, the cell consisted of a teflon cylinder with a big bore-hole in the centre and a small bore-hole at the side of the cylinder for the silver wire reference electrode. Two V2A pistons of 1 cm diameter served as current collectors (cell II). Pressure was applied in a hydraulic press.

The measuring electrodes (platinum and silver plates) were polished before use with fine γ-alumina powder.

For cyclic voltammetry, a Wenking-type potentiostat FR 0.5 (Fa. G.Bank, Göttingen), a voltage scan generator VSG 72 (G.Bank) and a Hewlett Packard *xy*-recorder were used. For impedance measurements a system described elsewhere was used [14].

3. Results

Because of the very low specific resistance of $RbAg_4I_5$, cyclic voltammetry seemed to be a valuable method for investigating some properties of the electrolyte and especially the electrode–electrolyte interphase. For that purpose a cell assembly: $Ag/RbAg_4I_5/Pt$ was built as cell I. Cyclic voltammograms obtained by dissolving silver from the silver measuring electrode are shown in Fig. 1.

In that case the cell was mounted by pressing the electrolyte to the counter electrode by means of a torque wrench. The cell was then opened again and the measuring electrode was pressed to the electrolyte by applying only a low pressure (fastening of the screw in the cell, which served as one electrode, by hand). The cyclic voltammogram exhibits a pronounced peak with a relatively small

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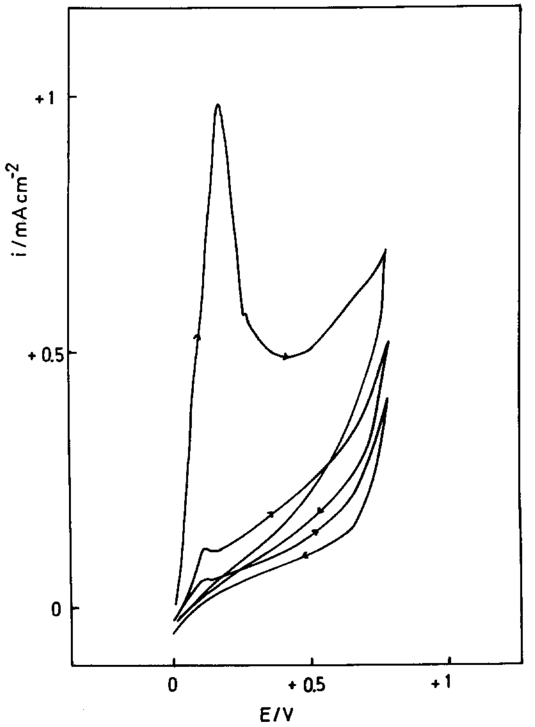

Fig. 1. Cyclic voltammograms of a cell: Ag/RbAg$_4$I$_5$/Pt. Scan rate, 100 mV s^{-1}; measuring electrode, Ag; reference electrode, Ag/AgI; no external pressure applied.

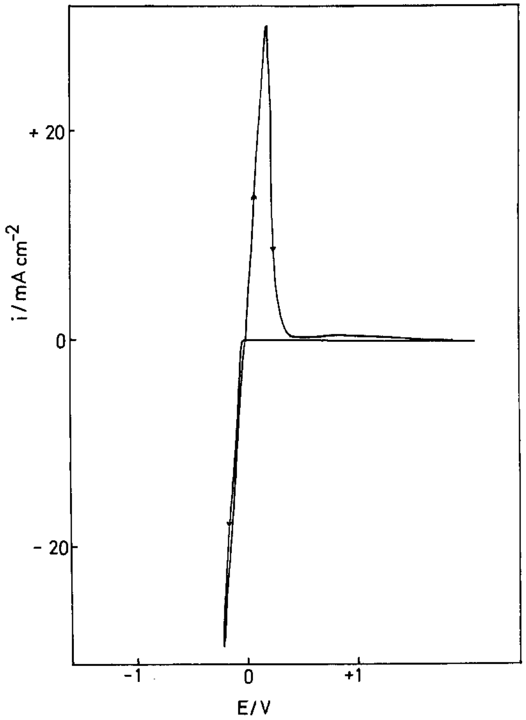

Fig. 2. Cyclic voltammogram of a cell: Ag/RbAg$_4$I$_5$/Pt. Scan rate, 5 mV s^{-1}; measuring electrode, Ag; reference electrode, Ag/AgI; no external pressure applied; starting point of the curve was the equilibrium potential of the cell; cathodic polarization was made prior to anodic polarization.

peak current during the first sweep and very much smaller peaks during the following sweeps. This interesting effect seems to be due to a contact loss between the silver measuring electrode and the solid electrolyte. The fact that only small amounts of charge are consumed until this contact loss occurs, suggests that there are only very few contact points between the electrode and the electrolyte. It may be easily proven that the observed effects are not due to the properties of the bulk electrolyte in recording voltammograms with a cathodic sweep prior to the silver dissolution.

If silver is deposited from the electrolyte prior to oxidation (under the same pressure conditions as used before) an oxidation of the deposited silver with high anodic current densities is possible (Fig. 2). In fact, even higher anodic current densities than those shown in Fig. 2 may be achieved (values up to 100 mA cm^{-2} were achieved during these experiments). Armstrong *et al.* [5] stated that freshly deposited silver is in a more active state than bulk silver. This is surely true, but it may not be the only reason why such high current densities are achieved during oxidation. In fact the main reason for this behaviour is most probably a large increase in contact area between the electrode and the electrolyte caused by the deposited silver.

A visual inspection of the silver electrode under the microscope after a cathodic sweep shows in fact a dendritic silver deposition. This explains the large increase in contact area between electrode and electrolyte that allows such high current densities.

The experimental results described above were obtained by using a full blocking arrangement: Pt/RbAg$_4$I$_5$/Pt or a blocking/non-blocking arrangement: Ag/RbAg$_4$I$_5$/Pt (with silver being the measuring electrode). If several sweeps are recorded, the curves coincide fully. The reaction at the counter electrode is an oxidation–reduction reaction of the iodine ions.

If a silver counter electrode is used: (Ag/RbAg$_4$I$_5$/Ag), the reaction at the counter electrode will be preferably silver oxidation and reduction. In that case, during the silver deposition at the measuring electrode and also during silver

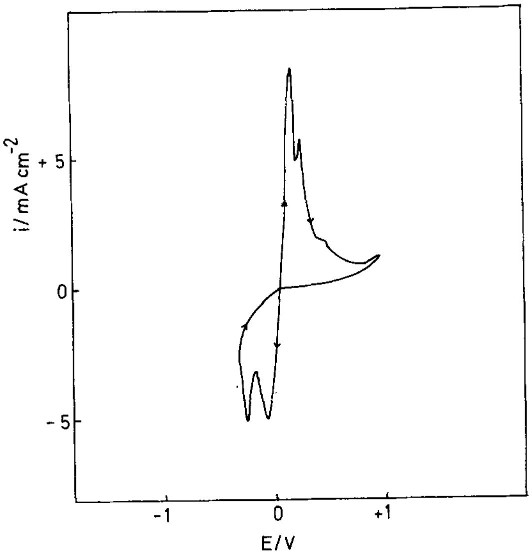

Fig. 3. Cyclic voltammogram of a cell: $Ag/RbAg_4I_5/Ag$. Scan rate, 0.05 mV s^{-1}; reference electrode, Ag/AgI; cathodic sweep was recorded first; no external pressure applied.

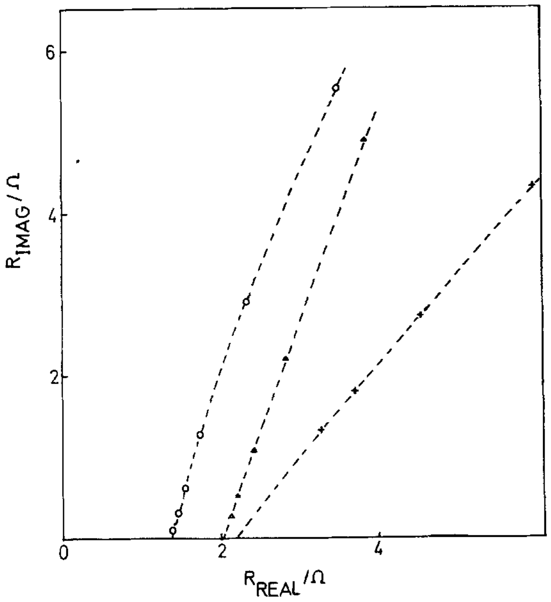

Fig. 4. High frequency parts of impedance diagrams of a cell $Ag/RbAg_4I_5/Ag$ under various pressures. +, After removing a pressure of 2600 bar; ▲, pressure 650 bar; o, pressure 2000 bar. Measured points correspond to frequencies of: 35 kHz, 20 kHz, 7.5 kHz, 3 kHz, 1 kHz, 400 Hz (the low pressure curves show only the four respectively five points with the highest frequencies).

oxidation, peaks in the cyclic voltammogram are obtained (Fig. 3).

This effect is most probably due to the hindered reaction at the counter electrode (contact loss) since it is not observed with a platinum counter electrode.

In any case the current densities achievable during cathodic silver deposition and redissolution are limited to some extent by the fact that short-circuiting of the cell due to dendritic silver deposition and/or by the iodine formed later may occur.

Because of these results it seemed to be of interest to observe the behaviour of the electrolyte–electrode interphase under pressure. For that purpose impedance spectra of a cell: $Ag/RbAg_4I_5/Ag$, were recorded under various pressures and the resistances determined by measuring the high frequency intercepts of the curves with the real axis (Fig. 4).

By these curves it may be easily demonstrated that the electrolyte resistances become smaller with increasing pressure. If the dependence of the overall cell resistance is plotted versus the applied pressure, an approximately exponential behaviour is observed (see the semi-logarithmic plot in Fig. 5).

The deviations from the straight line at low pressures are due to the fact that the electrolyte is not fully compressed. The decrease in the measured resistance with increasing pressure should be mainly due to an improved contact between the electrodes and the electrolyte. This assumption is confirmed by the fact that with increasing pressure the steepness of the impedance curves increases and the

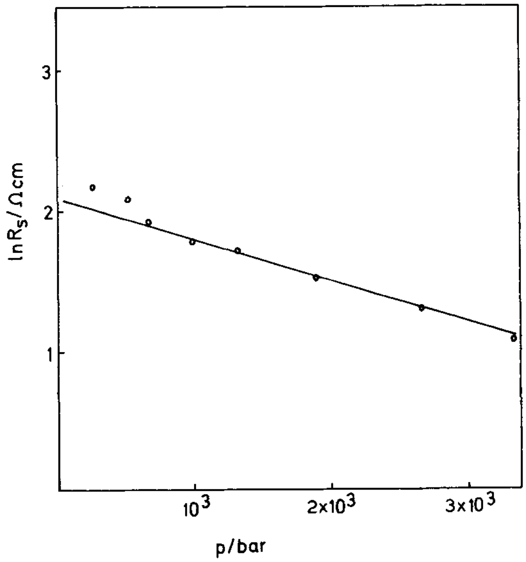

Fig. 5. Semi-logarithmic plot of the specific resistance of $RbAg_4I_5$ (measured in a cell arrangement: $Ag/RbAg_4I_5/Ag$) at different pressures.

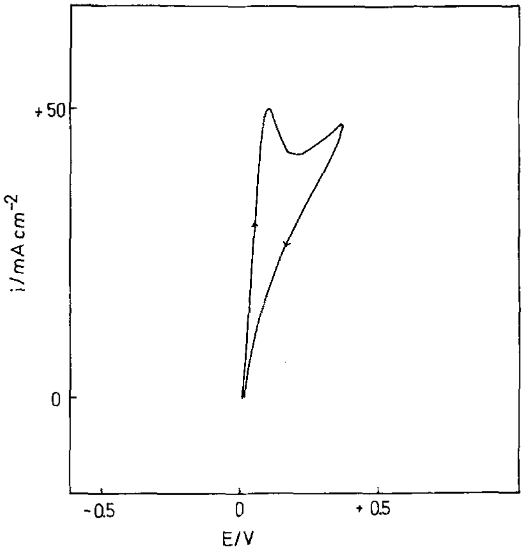

Fig. 6. Cyclic voltammogram of a cell: Ag/$RbAg_4I_5$/Pt. Scan rate, 100 mV s^{-1}; reference electrode, Ag/AgI; external pressure applied, 650 bar.

imaginary part decreases. According to Armstrong *et al.* [15] the shape of impedance curves is strongly influenced by, for example, surface roughness. Thus, increasing steepness should be due to increasing contact area. It is to be expected, however, that the influence of the contact area between electrode and electrolyte on the measured resistance value is only limited. This is due to the fact that relatively high frequencies are applied with small a.c. amplitudes so that no chemical reaction can occur during the measurements. Thus a few contact points are sufficient for these measurements. For further information, cyclic voltammograms were recorded under various pressures to detect any pressure dependence of the maximum peak currents. Fig. 6 shows that indeed a strong increase in current density during silver oxidation is observed if pressure is applied.

As in Fig. 1, subsequent cycles led to smaller currents being obtained. This fact is obviously also due to a contact loss between electrode and electrolyte. From these measurements maximum current densities (i_p-values) for silver oxidation in a completely solid state cell were determined. By measuring the i_p-values of the first sweep at various pressures (after each test a new cell assembly was built up to have similar conditions in each case), an exponential increase in current density was found as the pressure was increased. In Fig. 7 this

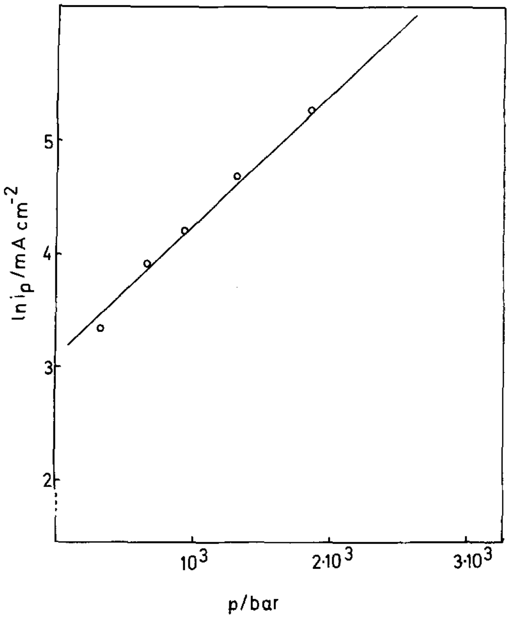

Fig. 7. Semi-logarithmic plot of i_p-values achieved during silver oxidation in a cell: Ag/$RbAg_4I_5$/Ag at different pressures.

is demonstrated by a semi-logarithmic plot of i_p-values versus the pressure.

Up to a pressure of about 750 bar the cyclic voltammograms are similar to those obtained at low pressure (Fig. 1) and exhibit a pronounced peak. At higher pressures *IR* behaviour becomes dominant and a shoulder instead of a peak is observed. The results (very high current densities during silver oxidation under pressure) indicate that the oxidation of silver in contact with a solid electrolyte in principle is not hindered for kinetic reasons. Hence the small current densities observed normally are not due to a kinetic hindrance of the silver oxidation, but to a bad contact and rapid contact loss during oxidation.

As mentioned earlier, dendritic silver deposition is obtained if only a low pressure is applied to the Ag/$RbAg_4I_5$ interphase. If pressure is applied (e.g. about 2000 bar), however, a smooth and shiny silver deposition at the side of the measuring electrode is observed. This deposited silver is not grown on the electrode surface but grown from the outer surface into the inner side of the electrolyte.

4. Discussion

From the experimental results some conclusions may be drawn:

(a) There is a simple relationship between the pressure applied and the specific resistance.

$$\ln R_{\mathrm{spec}} \propto p.$$

Because of the correlation between the measured resistance and the specific resistance:

$$R_{\mathrm{spec}} = RF/a$$

(a, thickness of the electrolyte in cm; F, contact area in cm^2) the following relationships are valid:

$$R_{\mathrm{spec}} \propto F$$

and correspondingly:

$$\ln F \propto p.$$

Whereas F generally is a fixed value, in the case discussed here it is assumed that F changes when the pressure changes, whereas R remains fixed (neglecting a slight pressure dependence of R which also may occur).

(b) A second correlation is observed between i_{p} and p according to:

$$\ln i_{\mathrm{p}} \propto p$$

From (a) and (b) it follows that:

$$i_{\mathrm{p}} \propto F$$

(c) Furthermore, the experiments show a linear dependence of the i_{p}-values on the square root of the scan rates ($\mathrm{V\,s^{-1}}$) in the cyclic voltammograms:

$$i_{\mathrm{p}} \propto \sqrt{(v)}.$$

From points (a)–(c) it may be concluded that:

$$i_{\mathrm{p}} = K\sqrt{(v)}F.$$

In this case it is assumed that K remains constant at increasing pressure. An important condition for this assumption is that kinetic factors do not significantly change during pressure application. The obtained results support the assumption that this is the case.

In the literature a value of $0.27\ \Omega^{-1}\ \mathrm{cm}^{-1}$ is reported for the $\mathrm{RbAg_4I_5}$ electrolyte [3]. This value is achieved at an applied pressure of about 2600 bar. From this observation it may be assumed that at this pressure the electrolyte is in full contact with the measuring electrodes. If it is further assumed that the electrode area corresponds to the geometric area ($F = 0.78\ \mathrm{cm}^2$; neglecting the unknown surface roughness) and if the i_{p}-value at this pressure, $i_{\mathrm{p}} = 437\ \mathrm{mA\ cm}^2$, (calculated from the extrapolated line in Fig. 7) is introduced into the formula, K may be calculated ($K = 1759$). By working with this value, it is possible to estimate values for the real contact area at various pressures (if the i_{p}-values at these pressures are measured).

It is obvious that the equation is somewhat oversimplified in that all kinetic parameters are reduced to one factor which is assumed to remain essentially unaffected by the pressure. Nevertheless, a rough estimation of the real contact area in the solid state cell ($\mathrm{Ag/RbAg_4I_5/Ag}$) should be possible. The results given in Fig. 8 show an exponential increase in the real contact area with increasing pressure.

From the results it may be concluded that high pressures (about 2600 bar) are required to obtain full contact between the solid electrode and the solid electrolyte.

This value, however, is valid only for the electrolyte described here. It may be assumed that the value depends strongly on the physical properties of the individual solid electrolyte, especially its

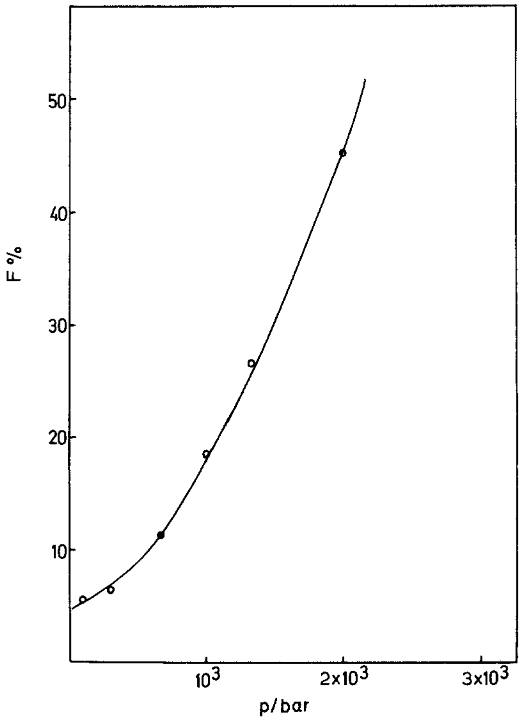

Fig. 8. Contact area in % (referred to geometric area of the electrode) in the solid state cell: $\mathrm{Ag/RbAg_4I_5/Ag}$ at varying pressures.

compressibility and smoothness. Furthermore, it is shown that during oxidation of the silver electrode a contact loss occurs very readily between the solid electrolyte and the solid electrode.

This behaviour is a severe hindrance in building solid state cells. In practice, a reformation of the contact is observed within a few minutes, even at low pressure, if only a short oxidation is made. This process, however, is too slow to allow the permanent passage of reasonable current densities, but nevertheless it may be fast enough to keep the contact in solid state cells established, if only low current drains (smaller than 1 mA cm^{-2} for example) are applied. Such low currents are delivered, for example, by the solid state lithium–iodine cells which are generally used for pacemakers.

Acknowledgement

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