OFFICE OF NAVAL RESEARCH

Impedance Studies of the Cell Ag/AgI/Ag Beta" Alumina/AgI/Ag

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Prepared for Publication

in

Solid State Ionics

Technische Universitat Wien
Institut fur Technische Elektrochemie
9, Getreidemarkt, 1060 Wein, Austria

July 1, 1988

AD-A198 254

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release and sale; its distribution is unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical report no. 15	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION Institut fur Technische Elektrochemie	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) 9 Getreidemarkt 1060 Wien, Austria		7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-83-K-0498

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION

11. TITLE (Include Security Classification)

Impedance Studies of the Cell Ag/AgI/Ag Beta" Alumina/AgI/Ag

12. PERSONAL AUTHOR(S)
M.W. Breiter, H. Drstak, M. Maly-Schreiber

13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 8/87 TO 8/88	14. DATE OF REPORT (Year, Month, Day) 1988, July 1	15. PAGE COUNT

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Solid electrolyte interfaces, AgI, Ag beta" alumina

Silver iodide,

silver

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.   SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete.

IMPEDANCE STUDIES OF THE CELL Ag/AgI/Ag BETA" ALUMINA/AgI/Ag

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ABSTRACT.

The construction of the cell Ag/AgI/Ag beta"alumina/AgI/Ag is described. The impedance of this cell was measured between 10^{-3} and 10^4 Hz at temperatures between 20 and 550°C. At temperatures below 100°C the cell impedance is determined to a large extent by the bulk resistance of the AgI layer and to a smaller extent by the impedance of the interface Ag/AgI. At temperatures between 160 and 350°C the impedance is controlled by the bulk resistance of the Ag beta alumina and an impedance due to contact problems between Ag and AgI. The bulk resistance of the beta"alumina becomes predominant between 350 and 550°C. A hindrance due to the transfer of silver ions from AgI to Ag beta"alumina was not observable in the whole temperature range.

INTRODUCTION.

The kinetics of the transfer of the conducting cation from a solid electrolyte 1 into an electrolyte 2 has been mainly studied when electrolyte 2 was a liquid. Silver ion conductors, especially AgI (1 - 4) and Ag_3SI (5,6), have been investigated in aqueous electrolytes. Organic electrolytes were used (7,8) for sodium beta aluminas.

Little work of a fundamental nature has been reported (9,10) for the case that both electrolytes are solids. Interest in the interface between two solid electrolytes with the same conducting ion exists for batteries (11) and sensors (9,12).

The symmetric cell Ag/AgI/Ag beta" alumina/AgI/Ag was chosen in this study. The two solid electrolytes are polycrystalline

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silver ion conductors. The Ag beta" alumina is not sensitive to water vapor (13). Impedance spectroscopy was applied in an attempt to obtain information on the ion transfer from one solid electrolyte to the other one.

EXPERIMENTAL SECTION.

Pieces (1 cm X 1 cm X 0.5 cm) were cut from bars of sodium beta" alumina obtained from Ceramatec Inc. as βetalyte material. They were ion exchanged in molten $AgNO_3$ at $250^{\circ}C$. The specimens of Ag beta" alumina were repeatedly dipped into and pulled out from molten AgI. Layers of AgI were formed on them in this way. The AgI layers were sanded off on the small rectangular surfaces. They were evened on the square surfaces and had thicknesses d between 0.01 and 0.15 cm. The contact between the AgI layer and the surface of Ag beta" alumina was checked by cross sectioning of a cell and looking at the interface by microscope. Good adherence was observed. Silver was sputtered onto the AgI surfaces. Then silver nets were attached by silver paint as leads. Rectangular pieces of aluminum oxyde with flat surfaces were pressed against the silver nets on both sides. Tungsten wire was wrapped around to hold the cell together at higher temperatures.

The Ag/AgI/Ag beta" alumina/AgI/Ag cells were kept inside a small furnace in a glass vessel purged by pure nitrogen. The temperature was measured by a thermocouple attached to one of the aluminum oxyde pieces and controlled by a temperature controller. The furnace was heated by DC current. For a new cell the temperature was increased stepwise from room temperature to $140^{\circ}C$ and decreased afterwards again. This is the temperature region in which the low temperature phases of AgI exist (14). Independent measurements of the bulk conductivity of pieces of AgI, prepared

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in a similar fashion, proved (15) that a mixture of the β and γ phase of AgI exists below 100°C and that a transformation to the β phase occurs at temperatures between 100 and 140°C. The measurements at temperatures between 160 and 550°C in the region of the α phase started at 550°C. The temperature was stepwise decreased at first and then increased again. Sufficient time was allowed between individual runs for the temperature equilibration.

The measurements of the cell impedance were carried out between 10^{-3} and 10^{4} Hz in the low temperature region and between 10^{-2} and 10^{4} Hz in the high temperature region. An automated impedance meter produced and sold by Zahner-elektrik/ West Germany was used. The reader is referred to ref.15 for details.

EXPERIMENTAL RESULTS.

The results of a measurement at 70°C and an AgI layer thickness of 0.05 cm are shown in Fig.1a as an example for the low temperature region in a Bode plot. For comparison similar data are given in Fig.1b for the cell Ag/AgI/Ag with d = 0.4 cm at 70°C. Squares denote the absolute value of Z_{cell} and asterisks the phase angle. Data at 300°C are presented in Fig.2 as an example for the high temperature region for the same cell.

A hysteresis phenomenon was observed in the region of the low temperature phases and between 160 and 350°C in that of the high temperature phase. The absolute values of the impedances at a given frequency are smaller with decreasing temperature than with increasing one.

DISCUSSION.

Since the upper frequency limit is 10^{4} Hz, the bulk impedan-

ces of AgI and Ag beta" alumina may be considered ohmic. The cell impedance is:

$$(1) \quad Z_{cell} = 2Z_{Ag/AgI} + 2Z_{AgI/beta"} + 2R_{AgI} + R_{beta"}$$

The interfaces were produced in the same way. Therefore a symmetric behavior is assumed. Computations of the bulk resistances from the conductivities, obtained by a four-probe measurement (15,16), and the geometric dimensions demonstrate for $d < 0.05$ cm:

a) $R_{AgI} > 10\ R_{beta"}$ for $20^{\circ}C < T < 100^{\circ}C$

b) R_{AgI} and $R_{beta"}$ comparable for $100^{\circ}C \le T \le 147^{\circ}C$

c) $R_{AgI} < 10\ R_{beta"}$ for the high temperature region

In principle the term $(2\ Z_{Ag/AgI} + R_{AgI})$ might be determined experimentally from impedance measurements (15) of the cell Ag/AgI/Ag with the same thickness of the AgI layer as the cell Ag/AgI/Ag beta"alumina/AgI/Ag at a given temperature and the same frequencies. The bulk resistances R_{AgI} and $R_{beta"}$ might be computed. The corrected impedance

$$(2) \quad Z_{cor} = Z_{cell} - 2Z_{Ag/AgI} - 2R_{AgI} - R_{beta"} = 2Z_{Ag/AgI}$$

contains the desired information. However, this approach only works in a qualitative fashion for two reasons:

d) It is not certain that the mixture of the two low temperature phases of AgI is the same in the production of the different cells. A compositional difference will strongly affect R_{AgI} since the γ phase is a much better conductor than the β phase (14). An effect of this type was confirmed by the measurements with cells of different thicknesses of the AgI layer. The cell impedance is nearly ohmic at 10^4 Hz and is approximately equal to R_{AgI}. However, the values of R_{AgI} did not depend upon d in a linear fashion because of the different composition of the mixtures.

e) The existence (15) of poor contacts between Ag and AgI in the high temperature region and the possibility of crack formation

during the phase transition from the low temperature phases to the high temperature phase introduce great uncertainty for a correction in this region. This is clearly seen between 160 and 350°C. The cell impedances at 10^4 Hz are practically ohmic, but differ by a factor of 3 for the three cells at 160°C. They should be equal to $R_{beta"}$.

The frequency dependence of the absolute value and the phase angle may be compared in a qualitative fashion for the cells Ag/AgI/Ag beta"alumina/AgI/Ag and Ag/AgI/Ag. They are similar. It is suggested on the basis of this result that the frequency dependence is mainly due to $Z_{Ag/AgI}$ in both cases. The interface Ag/AgI beta"alumina does not contribute much to Z_{cell}. The latter conclusion is confirmed by the impedance data between 10^3 and 10^4 Hz. The phase angle approaches relatively small values for the cell Ag/AgI/Ag beta"alumina/AgI/Ag. The ohmic part of $Z_{cell'}$ computed in a series circuit, is close to the value of R_{AgI}.

The impedance data in the low temperature region were analysed, using the network in Fig.3. The meaning of the components of this network is given below the figure. Only the interface Ag/AgI is considered. A software program, delivered together with the automated impedance meter, finds the values of the components which produce the optimal fit of the frequency dependence of the absolute value and the phase angle between the network and the experimental data. The results of the optimisation are represented by solid lines in Fig.1a and Fig.1b. While it is possible to approximate the absolute values in a satisfactory fashion, this is not achievable for the phase angle. It is suggested that the latter effect is due to the implicit assumption of homogenoeus surfaces in the network of Fig.3. Many networks, probably of the

type in Fig.3, in parallel would approximate heterogeneous surfaces. The superposition of many time constants would yield a relatively flat curve for the phase angle as function of frequency as it is seen in Fig.1a and Fig.1b. Similar results were obtained at the other temperatures in this region.

A discussion of the data between 160 and 350^OC is difficult because of the mentioned influence of the AgI layer on Z_{cell}. Such an influence should not exist according to the estimate given under point c. The contribution of contact problems between Ag and AgI is considered responsible. The reader is referred to the discussion in ref.15.

The impedance data between 350 and 550^OC are relatively simple. The absolute value is nearly independent of frequency between 10^{-2} and 10^4 Hz and practically equal to $R_{beta"}$. The phase angle is very small. The contribution of the other components in Z_{cell} (compare Eq.1) is negligible relative to that of $R_{beta"}$.

ACKNOWLEDGEMENT.

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Figure Captions.

Fig.1 : Impedance spectra at 70°C in Bode plots of the cells (a) Ag/AgI/Ag beta" alumina/AgI/Ag and (b) Ag/AgI/Ag.

Fig.2 : Impedance spectrum of the cell Ag/AgI/Ag beta alumina/AgI/Ag at 300°C.
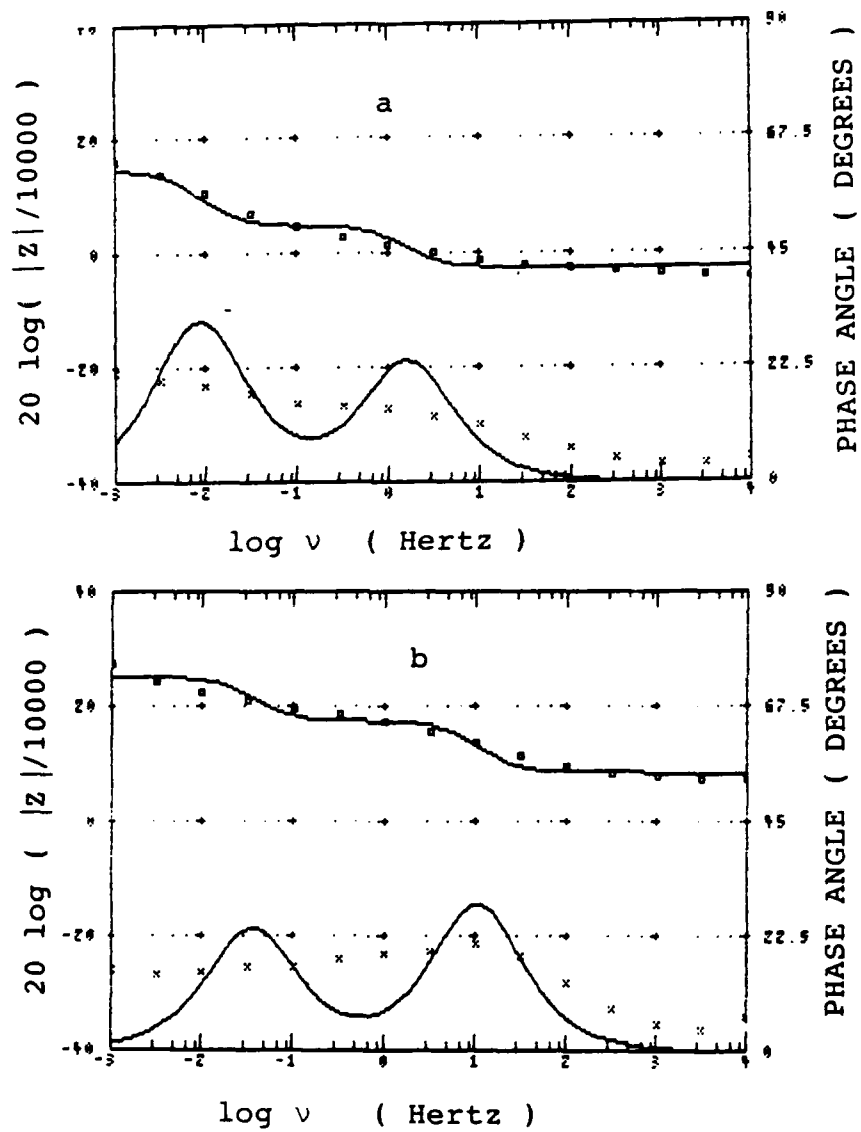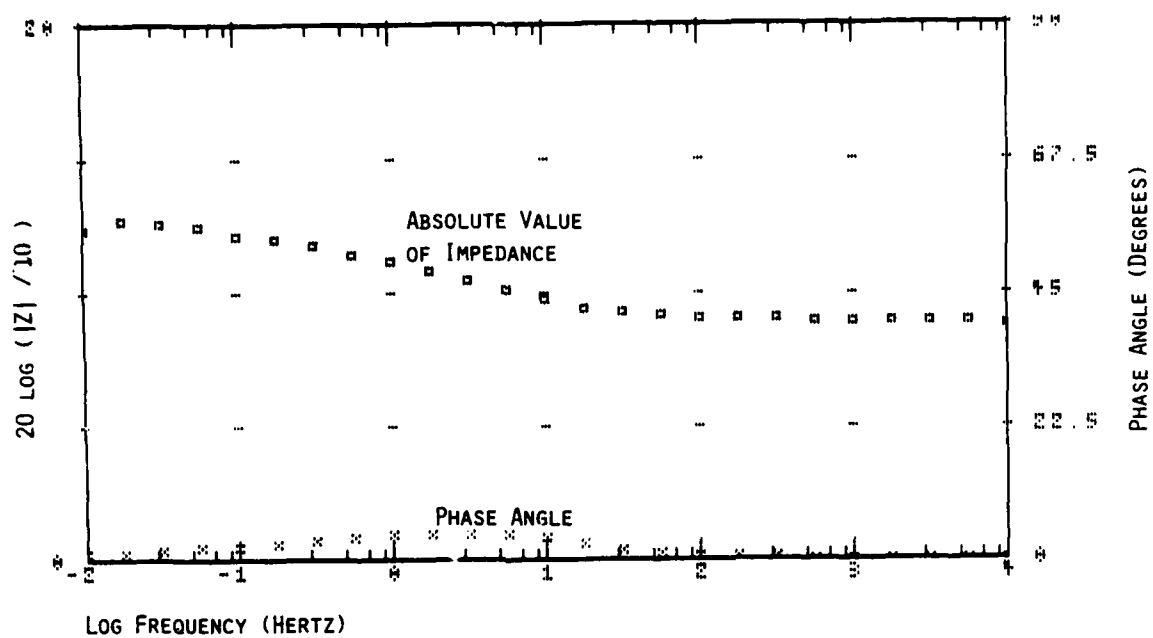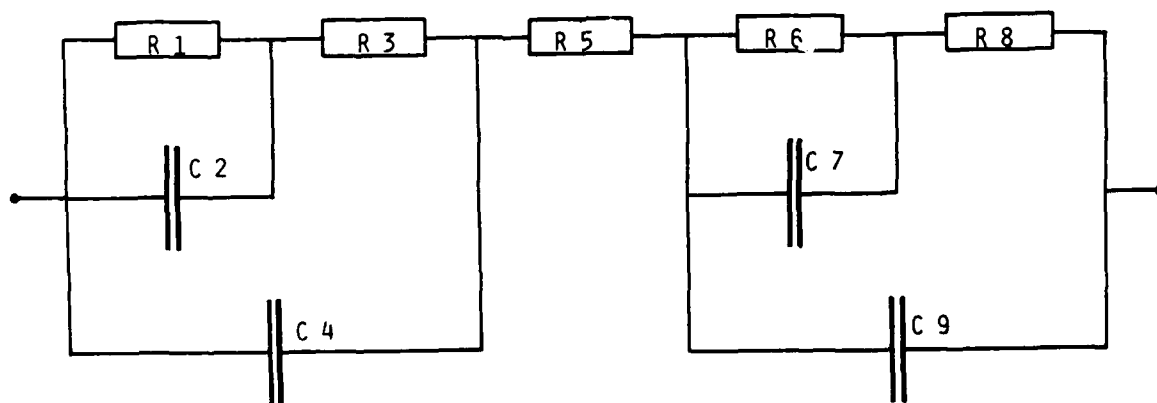
Fig.3 : Network for the cell.

Fig.1

Fig.2

R 5.........RESISTANCE OF SOLID ELECTROLYTE
R 1, R 6.....REACTION RESISTANCE
R 3, R 8.....DISCHARGE RESISTANCE
C 2, C 7.....REACTION CAPACITANCE
C 4, C 9.....DOUBLE LAYER CAPACITANCE

Fig.3