



••

. . . . . .

1

•

MICROCOPY RESOLUTION TEST CHART NATIONAL BUREAU OF STANDARDS-1963-A

# UNG FILE CORY

AD-A183 110

# OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0498 R&T Code 413d011---02

Technical Report No. 11

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

by

M.W. Breiter, H. Drstak and M. Maly-Schreiber

Prepared for Publication

in the

Journal of Electroanalytical Chemistry

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

July 1, 1987



4

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

## **Unclassified**

• ?

SECURITY CLASSIFICATION OF THIS PAGE

# ADA183/10

1EP	ORT	DOC	JMENT	ΓΑΤΙ	ION	PAGE
-----	-----	-----	-------	------	-----	------

	REPORT DOCUM	ENTATION PAG				
14 REPORT SECURITY CLASSIFICATION	16. RESTRICTIVE N	LARKINGS				
2. SECURITY CLASSIFICATION AUTHORITY		J. DISTRIBUTION	VAILABILITY O	FREPORT		
-		This docu	ment has	been appro	ved	
3. DECLASSIFICATION/DOWNGRADING SCHED	DULE	for public	c release	and sale	;	
		<u>its distr</u>	<u>ibution i</u>	<u>s unlimite</u>	ed	
4. PERFORMING ORGANIZATION REPORT NUM	<b>B</b> FH(3)	5. MONITORING ORGANIZATION REPORT NUMBER(S)				
lechnical Report No. 11						
SA NAME OF PERFORMING ORGANIZATION	54. OFFICE SYMBOL (If applicable)	74. NAME OF MONITORING ORGANIZATION				
Institut für Technische	1	Office of Naval Research				
Ge. ADDRESS (City, State and ZIP Code)	<u></u>	75. ADDRESS (City, State and ZIP Code)				
5 Getreidemarkt		800 North Ouingy Street				
1060 Wien/ Austria		Arlington, VA 22217				
	· · · · · · · · · · · · · · · · · · ·					
S. NAME OF FUNDING/SPONSORING	Bb. OFFICE SYMBOL	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER				
	,.,	N00014-83-K-0498				
Be ADDRESS (City State and ZIP Code)		10 SOURCE OF FU				
		PROGRAM	PROJECT TASK WORK UNIT			
		ELEMENT NO.	NO.	NO.	NO.	
			1	A dendify by block number, and the sodium and the sodium an		
11. TITLE (Include Security Classification)			TRICTIVE MARKINGS   INSUTION/AVAILABILITY OF REPORT   S document has been approved public release and sale; distribution is unlimited. TORING ORGANIZATION REPORT NUMBER(S)   # OF MONITORING ORGANIZATION fice of Naval Research   RESS (City, Sum and ZIP Code)   0 North Quincy Street lington, VA 22217   UNREMENT INSTRUMENT IDENTIFICATION NUMBER   0014-83-K-0498   REC OF FUNDING NOS. MARAM   PROJECT   TASK NO.   NO.   Y. Chem.   NO.   NO.			
Impedance Studies of the	Cell Ag/Ag	I		l <u> </u>	_	
M.W.Breiter, H.Drstak an	nd M.Malv-Sch	reiber				
134 TYPE OF REPORT 136. TIME C	OVERED	14. DATE OF REPORT (Yr., Ma., Day) 15. PARE COUNT				
Technical Report FROM Sep	1987, July 1		14	· · · · · · · · · · · · · · · · · · ·		
16. SUPPLEMENTARY NOTATION						
Submitted for publication	1 to J.Electro	oanalyt.Cher	n.			
17. COSATI CODES	18. SUBJECT TERMS (C	ontinue on reverse if ne	cessary and identi	ly by block number	)	
FIELD GROUP SUB. GR.	Solid elec	trolyte, bet	a"alumin	a, impedan	ice	
	spectra, in	nterface <i>nl nl nl</i>				
				//		
Measurements of the cell	impedance way	$re$ carried $\lambda$	$\Lambda$	n = 1	norsture	
between 25 and 450°C at 1	frequencies be	etween La	and Lat	Ha. The en	rfaces	
of the solid electrolyte	which was ob	tained by ex	changing	the sodiu	m	
ions of the starting mate	rial, Na beta	aCalumina fi	com Ceram	atec Inc.,	by	
silver ions in molten Agi	₩3 were eithe	er polished	or sawerc	ut. Silver	. –	
electrodes were attached	bý silver pa:	int after ap	plying t	he initial		
of a blocking ploctrode	ig. The silver	r elctrodes	display	the behavi	or	
about 200 C. This behavio	n a wide Ire( )r is clearer	quency range	at temp	eratures b	elow	
faces. The sawacut surfac	ces show an in	termediate	behavior	hetween b	locking	
and non-blocking electrod	les. A transit	tion from bl	locking to	o non-bloc	king	
electrode occurs between	150 and $200^{\circ}$	for both t	ypes of	surfaces.	3	
The impedance data are ar	nalyzed in the	e lower temp	perature	range by a	n	
20. DISTRIBUTION/AVAILABILITY OF ABSTRAC	T	21. ABSTRACT SECU	AITY CLASSIFIC	CATION		
UNCLASSIFIED/UNLIMITED A SAME AS RPT.	Unclassified					
22. NAME OF RESPONSIBLE INDIVIDUAL		226. TELEPHONE N	MBER	22c. OFFICE SYM	30L	
M.W.Breiter	Vienna:588(	1 4762				
D FORM 1473 83 APR	EDITION OF 1 JAN 73 4	S OBSOLETE	······			
	a para a para di mana di		SECURI	Y CLASSIFICATIO	N OF THIS PAGE	

Unclassified

Developments in the termine

## Impedance Studies of the Cell Ag/Ag Beta"Alumina/Ag \*

## M.W.Breiter, H.Drstak and M.Maly-Schreiber

Institut für Technische Elektrochemie, TU Wien, 9 Getreidemarkt, 1060 Wien/Austria

## ABSTRACT.

Measurements of the cell impedance were carried out at constant temperature between 25 and 450°C at frequencies between  $10^{-2}$  and  $10^{4}$  Hz. The surfaces of the solid electrolyte which was obtained by exchanging the sodium ions of the starting material, Na beta"alumina from Ceramatec Inc., by silver ions in molten AgNO, were either polished or saw-cut. Silver electrodes were attached by silver paint after applying the initial silver layer by sputtering. The silver electrodes display the behavior of a blocking electrode in a wide frequency range at temperatures below about 200°C. This behavior is clearer pronounced on the polished surfaces. The saw-cut surfaces show an intermediate behavior between blocking and non-blocking electrodes. Α transition from blocking to non-blocking electrodes occurs between 150 and about 200°C for both types of surfaces. The impedance data are analyzed in the lower temperature range by an Accession For analogue network.

		••	
NTIS	GRALI	CT	
DTIC	TAB	<b>A</b>	
Unann	ounced	ñ	
Just1	ficatio	on	_
By	4	~ 1	
DIELF	IDUCIO	a/	
Aval	labilit	ty Codes	
_	Ava11	and/or	
Dist	Spec	ial	
		1	- Ii
<b>Л</b> /	ł	1	
	1	1	

Years and

\* Dedicated to Prof.H.Gerischer

#### INTRODUCTION.

The impedance of the cell Ag/Ag beta"alumina/Ag was investigated for the following reasons:

1) It is a relatively simple system, involving a solid electrolyte of the beta alumina  $group^1$  with the one-valent silver ion as the conducting species and silver metal as electrodes. The cell is symmetric with respect to the electrodes. Information about the behavior of the interface Ag/Ag beta alumina as a function of temperature should be deducible.

2) When using silver contacts in four-probe measurements<sup>2</sup> of the ionic conductivity of Ag beta "alumina at  $10^3$  Hz, a change in the properties of the contacts was observed to occur in the temperature range between about 100 and 200°C. This indicated that a change in the properties of the interface, possibly the transition from silver as a blocking electrode to silver as a non-blocking electrode, occurs.

3) Since Ag beta "alumina does not pick up water to a noticeable extent<sup>3,4</sup>, the interpretation of the impedance measurements is not complicated by additional electrochemical processes, due to water or hydronium ions<sup>5</sup>.

Impedance measurements<sup>6</sup> proved very useful in the study of electrode kinetics in aqueous solutions. An excellent review of the application of this technique to solid electrolytes is given in ref.7. Here the results of the impedance measurements with the said cell in the frequency range  $10^{-2}$  to  $10^{4}$  Hz and temperature range 25 to  $450^{\circ}$ C will be presented. Two types of surfaces of the solid electrolyte were used: saw-cut and polished. The solid electrolyte was polycrystalline.

#### EXPERIMENTAL SECTION.

Pieces of rectangular cross section ( lcm X lcm ) and a thickness of about 0.5 cm were cut from bars of polycrystalline Na beta" alumina, supplied by Ceramatec Inc. The nominal composition of this starting material was: 90.4% Al<sub>2</sub>O<sub>2</sub>, 8.85% Na<sub>2</sub>O, 0.75% Li<sub>2</sub>O. The sodium ions were replaced by silver ions by immersing the samples for 24 hours in molten  $AgNO_{3}$  at 250 $^{O}C$ . The completeness of the ion exchange was monitored by the weight As demonstrated recently<sup>8</sup>, the weight change allows to change. compute the extent of exchange in a good approximation for polycrystalline Ag beta"alumina.

Some of the exchanged samples were polished on both large sides to 1 µm. Silver films were sputtered onto these sides of the polished and unpolished specimens. The thickness of these films was 10 to 50 nm. Silver paint was applied afterwards. The silver paint dried for 24 hours in air and for 24 hours at about 200°C. Silver nets were attached by silver paint, using the same drying process as before. The nets were cut in such a way that they consisted of square pieces (lcm X lcm) for contacts and rectangular pieces (0.2cm X 1cm) for leads. Flat pieces of alpha alumina were pressed against the silver nets. Tungsten wire was wrapped around the cell to keep it together. The rectangular pieces of silver net were hooked up to the relatively thick Ag wires of the measuring cell by brass connections with screws. A schematic diagram of the cell and a photo of the actual cell are shown in Fig.1.

The measurements were carried out inside a Pyrex glass vessel, flushed by nitrogen. The glass vessel had a lid with a removable large joint through which the silver wires were

introduced by smaller joints. The removable large joint allowed to mount the Ag/Ag beta"alumina/Ag cell on the outside. The glass vessel was inside a small furnace heated by DC current. The furnace and the lid of the glass vessel were well insulated. The temperature was maintained at a desired value by a temperature controller. Sufficient time was allowed for temperature equilibration between individual runs. The use of DC current significantly reduced the noise which is introduced from the net in the case of AC heating.

The meassurements of the cell impedance were carried out at constant temperature, starting out with room temperature and subsequently going to increasingly higher temperatures. The automated impedance meter IM 5E, produced and sold by Zahnerelektrik in West Germany, was employed. The frequency range covered  $10^{-2}$  to  $10^4$  Hz in this study.

#### EXPERIMENTAL RESULTS.

Impedance spectra for the cell Ag/Ag beta"alumina/Ag with polished surfaces of the solid electrolyte are shown for 50, 250 and 400°C in Fig.2. The data are presented in a Bode plot. The automated impedance meter yields the data in this form. An attempt to obtain the data in a Cole-Cole plot was not undertaken. At present it requires the manual transfer of the data to another computer by which the Cole-Cole plot is produced. Work is in progress to develop a technique of automated transfer of the data.

The respective data for the said cell with saw-cut surfaces of the solid electrolyte are contained in Fig.3. As in Fig.2 the three temperatures were chosen as representative for the

temperature dependence of the behavior of the interface.

DISCUSSION.

General Considerations.

An attempt will be made to interprete the frequency dependence of the impedance of the cell Ag/Ag beta"alumina/Ag at constant temperature by the network in Fig.4. The meaning of the ohmic and capacitive elements in this network will be given later. The following basic assumptions are involved:

a) The surfaces forming the interfaces Ag/Ag beta"alumina are smooth and homogeneous.

b) The frequency range is chosen such that the bulk impedance<sup>7</sup> can be represented by the ohmic resistance R5, e.g. the contribution of the capacitive component of the bulk impedance, due to grain boundaries, is negligible.

c) The absolute value of the cell impedance is low enough that the contribution of the geometric cell capacitance<sup>7</sup> which is parallel to R5 is negligible.

The assumptions b) and c) can be fulfilled by the choice of appropriate frequency ranges. Since Ag beta"alumina is a relatively good ionic conductor the condition b) holds for frequencies below 10<sup>4</sup> Hz. To check the fulfilment of condition c) frequency dependence of different resistors with the low inductance was measured as a function of frequency by the impedance meter. The phase shift due to capacitive effects was small at frequencies between  $10^3$  and  $10^4$  Hz if the resistance remained below 10  $^{4}\,\Omega$  . This implies that the geometric capacitance is negligible in the frequency range of this study. It should be pointed out that the contribution of the geometric capacitance is inversely proportional to the frequency. Therefore larger absolute values of the cell impedance can be measured at lower frequencies. The assumption a) is very questionable because the polycrystalline Ag beta" alumina itself is not a homogeneous material. It contains a small percentage of the beta alumina phase and of aluminate. In addition there are closed- ended pores originating on the surface<sup>8</sup>. The applicability of assumption a) to the present system will be discussed in connection with the experimental results.

The network in Fig.4 is useful for two special cases:

d) Blocking electrode.

e) Non-blocking electrode.

The meaning of the components in the network differs for cases d) and e). In case d) an electrochemical reaction does not occur to a noticeable extent. The adsorption capacitances C2 and C7 are small. The sums (R1 + R3) and (R6 + R8) correspond to the ohmic component of the double layer impedances. C4 and C9 are the double layer capacitances. Models which take account of the roughness of a surface have been suggested<sup>7,9</sup>. In addition, a distribution of the sites was considered<sup>9</sup>.

ALEXIST TROSSESS NUMBER OF A SUSSENCE AND A SUSSENCE AND AND AND A SUSSENCE AND A SUSSENCE AND A SUSSENCE AND A

In case e) the influence of the ohmic component of the double layer impedance is neglected. C4 and C9 have the same meaning. R3 and R8 are charge transfer resistances of the reaction :

(1)  $Ag^+ + e^- = Ag_{ad}$ 

R1 and R6 represent the resistances due to a possible adsorption reaction involving silver ad-atoms in the present study.

The intermediate case between d) and e) is difficult to describe by the network in Fig.4. It is not certain how to take account of the ohmic component of the double layer impedance. It

will be shown subsequent y that the case d) corresponds in a first approximation to measurements in a certain frequency range at temperatures below about  $200^{\circ}$ C. At temperature above  $200^{\circ}$ C the case e) is applicable. Therefore the subsequent discussion is divided into a section dealing with the measurements below  $200^{\circ}$ C and another section for higher temperatures.

Behavior of the Electrochemical Cell below 200<sup>0</sup>C.

The data at  $50^{\circ}$ C are presented in Fig.2 as an example for the behavior of the cell Ag/Ag beta "alumina/Ag with polished surfaces at temperatures below about  $200^{\circ}$ C. The cell impedance  $Z_{cell}$  can be approximated in a wide frequency range (  $10^{\circ}$  to  $10^{3}$ Hz ) by the equation:

(2)  $Z_{cell} = B(j\omega)^{-n}$ 

Here B is a constant and n has values between 0 and 1. From a practical point of view the n values varied<sup>9</sup> between about 0.9 at temperature and 0.6 at 400°C for the system Pt/Ag room beta"alumina/Pt. Usually a double-logarithmic plot of ohmic and capacitive component of the impedance versus the frequency is employed in the verification of Eq.2. The double-logarithmic plot is not as sensitive as the plots of phase angle versus logarithm of frequency of this study. A look at the data in Fig.2 at  $50^{\circ}$ C demonstrates the latter point. The absolute value of Z<sub>cell</sub> can be approximated by a linear function in a wider frequency range than the range in which the phase angle is nearly constant. The determination of n from the data between  $10^{\circ}$  and  $10^{3}$  Hz in Fig.2 leads to 0.90. This value is close to the one quoted in ref.9 for the system Pt/Ag beta"alumina/Pt with polished polycrystalline surfaces. Similarly, the present value of the constant D,

defined in table 1 of ref.9, differs only by a factor 2 from the one quoted there. The great sensitivity of the Bode plots also revealed that the wide frequency range of nearly constant phase angle, observed at 25 and  $50^{\circ}$ C, splits into two regions at 100 and  $150^{\circ}$ C. The phase angles are nearly constant in each of the two regions, but differ somewhat. It was already concluded<sup>9</sup> from the temperature dependence of n that the surface is composed of many areas with different n values. This conclusion is confirmed here.

As it is discussed extensively in ref.9 in which references to earlier work of the same nature can be found, the frequency dependence in Eq.2 is characteristic for that of the interface between a blocking electrode and a solid electrolyte. Possible models which consider the effect of the surface roughness and lead to Eq.2 are described there<sup>9</sup>.

Systematic deviations in the ohmic component of the cell impedance from the behavior according to Eq.2 are observable at frequencies between  $10^3$  and  $10^4$  Hz in Fig.2 at  $50^{\circ}$ C. As for the cell Pt/Ag beta"alumina/Pt in ref.9 the deviations at high frequencies are ascribable to the fact that the ohmic component approaches the DC resistance of the solid electrolyte, e.g. R5 in Fig.4.

The inaccuracy of the determination of the ohmic component at low frequencies and phase angles close to  $90^{\circ}$  was considered responsible<sup>9</sup> for the deviations in the low frequency range ( $10^{-1}$ to  $10^{1}$  Hz) in the system Pt/Ag beta"alumina/Pt. The present measurements on the system Ag/Ag beta"alumina/Ag suggest that the deviations in the low frequency range are of a systematic nature and cannot only be assigned to inaccuracies. The phase angle decreases rapidly from a value close to  $90^{\circ}$  to a

smaller value. This deviation of the experimental data from Eq.2 is discussed in the next paragraph. It should be pointed out that the employment of Ag electrodes is also mentioned in ref.9. However, experimental data or information on the type of cells with Ag electrodes are not given.

2.

The network in Fig.4 corresponds to n = 1 of Eq.2. It might hold approximately for the data in Fig.2 at 50°C since the measurements between  $10^1$  and  $10^3$  Hz demonstrate a nearly constant phase angle close to 90° and the deviations at frequencies above 10<sup>3</sup> Hz can be attributed to R5. Assuming that the impedance of the double layer can also be described in a first approximation by a capacitance at low frequencies, an attempt was made to the values of the components of the network in Fig.4. determine This was done by an optimization program delivered by Zahner-Every second experimental point was used in elektrik. the optimization. Principally, the question arises to what extent the determination of a large number of parameters (here : 9) from the experimental data can be meaningful for the validation of a model. Fortunately, the number of parameters reduces itself here. Owing to the similar preparation of the interfaces it can be assumed that the cell is symmetric, e.g. R1 = R6, R3 = R8, C2 = A correct optimization should give numerical values for the C9. components of the network reflecting the said symmetry. Finally it can be estimated if R5 has a reasonable value by comparing it with the value for the bulk resistance, computed from the geometric dimensions of the sample and four-probe the conductivity. The word "estimated" was used here since the measurements<sup>2</sup> appearance of a phase angle during the four-probe of the bulk conductivity does not allow the exact determination at low temperatures.

The result of the computation is shown by the solid curve in Fig.5. An approximate fit is achievable. However, the theoretical curve shows a small peak which does not exist at low frequencies in the experimental data. Symmetrical elements have The value of R5 ( bulk resistance ) is similar values. reasonable. The values for the double layer capacitance ( C4 and C9 ) are small with  $3 \cdot 10^{-8}$  F/cm<sup>2</sup> . The values of C2 and C7 with  $6 \cdot 10^{-8}$  F/cm<sup>2</sup> are comparable to those for the double layer capacitance and indicate in the frame of the model that there are few Ag ad-atoms. Results similar to those in Fig.5 were obtained when applying the optimization program to other measurements below about 200°C. The following interpretation is advanced: The interface Ag/Ag beta"alumina with polished surfaces displays the behavior of a blocking electrode at frequencies between 10<sup>0</sup> and  $10^4$  Hz in the said temperature range. At frequencies between  $10^{-2}$ and 10<sup>0</sup> Hz the effect of reaction 1 has to be considered. Probably the behavior corresponds to the intermediate situation between the limiting cases d) and e).

The results in Fig.3 at  $50^{\circ}$ C were obtained with saw-cut surfaces. The data might be described in a rough approximation between  $10^{-2}$  and  $10^{1}$  Hz by Eq.2 with a value of n close to 0.3. However, judging from the relatively small change of the values of n in Table 1 of ref.9 for the transition from a polished to a saw-cut polycrystalline surface, the change from n = 0.9 to n = 0.3 appears too large. Computations with the optimization program for the network in Fig.2 were also carried out. They yielded the result that the values for symmetrical elements were not numerically close to each other for all the measurements below  $200^{\circ}$ C. The cell Ag/Ag beta" alumina/Ag with saw-cut surfaces

displays a more complicated behavior than that with polished surfaces. It is suggested that the "asymmetrical" behavior, indicated by the optimization program, reflects the presence of different sites on each of the two electrolyte surfaces and not a difference in the two interfaces. The superposition of many networks of the type in Fig.4 will lead to a flat curve for the phase angle. The absence of surface homogeneity for the saw-cut is responsible for the observed behavior. Since the surfaces surfaces are larger in the case of saw-cutting than of polishing, the experimental data demonstrate a stronger participation of reaction 1 in the former case. On the basis of the preceding discussion the results in Fig.3 at 50<sup>0</sup>C may be interpreted in a qualitative fashion. The intermediate case between blocking and non-blocking electrode is already observable at higher frequencies (  $10^1$  Hz ) on the saw-cut surfaces. The increase of the phase angle between  $10^1$  and  $10^3$  Hz indicates the transition to a more capacitive behavior as it is seen at lower frequencies on the polished surfaces ( compare Fig.2, 50°C ). The influence of the bulk resistance (R5) is recognizable between  $10^3$  and  $10^4$ Hz.

Behavior of the Electrochemical Cell above 200°C.

1334-130

A rapid transition from the behavior of the cell impedance in Fig.2 at  $50^{\circ}$ C to that in Fig.2 at  $250^{\circ}$ C occurs between 150 and  $200^{\circ}$ C for the cell with polished surfaces. It is this type of transition which becomes noticeable in the same temperature range during the four-probe measurements of the ionic conductivity of Ag beta alumina with silver contacts for the voltage probes<sup>2</sup> at  $10^{3}$  Hz. While the phase angle amounted to  $45^{\circ}$  at  $10^{-1}$  Hz at a

temperature of 50°C, it reaches 45° at about 200 Hz at 250°C. The impedance displays the more capacitive behavior cell at considerably larger frequencies. The decrease of the phase angle due to the influence of the bulk resistance occurs at higher frequencies than 10<sup>4</sup> Hz and is therefore not observable in Fig.2 at 250<sup>0</sup>C. The absolute value of the cell impedance decreases in the frequency range of more capacitive behavior. However, the ohmic component of the cell impedance does not yet reach the value of the bulk resistance, computed from the geometric dimensions and the four-probe conductivity. The transition to more capacitive behavior for the cell impedance moves to higher frequencies with increasing temperature and is not visible in Fig.2 at 400°C any more. The experimental results suggest that the change of the properties of the cell impedance between 150 and 200°C reflects the transition from the predominance of the behavior of a blocking electrode in a wide frequency range to the predominance of that of a non-blocking electrode.

The absence of the frequency range in which R5, C4 and C9 of the network in Fig.4 should make a large contribution reduces the applicability of this network for temperatures above  $200^{\circ}$ C. Nevertheless the optimization program was employed to see if a systematic trend was observable. The values for symmetrical elements turned out to be the same in the whole temperature range. The values of the double layer capacitance remained relatively low. The values of the pseudocpacitances C2 and C7 became too large above  $250^{\circ}$ C, when compared with the values of the double layer capacitance R5 was found larger than the computed bulk resistance. The results of the computations confirm the statement in the beginning of this

paragraph.

The change in the shape of the frequency spectrum of the cell impedance, observed between 150 and 200°C on cells with sawcut surfaces of the solid electrolyte, is different from the change for cells with polished surfaces. Essentially, the phase angle becomes nearly independent of frequency and assumes relatively small values. The effect of the bulk resistance of the solid electrolyte on the absolute value of 2 ~ 1 ] clearly is recognizable up to 300°C. Then the absolute value of the impedance does not vary much with frequency any more. An analysis of the experimental data by the network in Fig.4 becomes difficult with increasing temperature because of the small values of the phase angle at larger temperatures. It is interesting to note that the optimization program begins to yield the same values for symmetrical components of the network, starting at 200°C. The resistance R5 makes a relatively large contribution to the total impedance at 200 and 250°C. Therefore the network analysis gives the bulk resistance of the solid electrolyte in a first approximation. Above 300°C the ohmic component of the cell impedance at 10<sup>4</sup> Hz is very close to the value of the bulk resistance, computed from the dimensions and the four-probe conductivity. The cells with saw-cut surfaces display the behavior of a cell with non-blocking electrodes.

3

#### ACKNOWLEDGENENT

The research was supported in part by the U.S.Office of Naval Research.

#### **REFERENCES**.

1. See G.C.Farrington and J.L.Briant, Science 204 (1979) 1371

2. P.Linhardt, M.Maly-Schreiber and M.W.Breiter, Proc. 6th International Symposium on Metallurgy and Materials Science, F.W.Poulsen, N.Hessel Hendersen, K.Clausen, S.Skaarup and O.Toft Sorensen, eds., RISO National Laboratory, Roskilde, 1985, p.475

3. J.Garbarczyk,, W.Jakubowski and H.Wasiucionek, Solid State Ionics 9 & 10 (1983) 249

4. P.Linhardt, PhD Thesis, TU Wien, 1986

5. K.Jasczynski, J.Zielinski, J.Dabkowski and S.Minc, Solid State Ionics 15 (1985) 9

6. H.Gerischer, Z.physik.Chem. 198 (1951) 286; ibid. 201 (1952) 55, Z.physik.Chem.N.F. 1 (1954) 278

7. W.I.Archer and R.D.Armstrong, Specialist Periodical Reports, The Chemical Society,, London-Electrochemistry 7 (1980) 157

8. M.Maly-Schreiber, P.Linhardt and M.W.Breiter, Solid State Ionics in print

9. J.B.Bates,, J.C.Wang and Y.T.Chu, ibid. 18 & 19 (1986) 1045

FIGURE CAPTIONS.

Fig.1: Setup of the cell Ag/Ag beta"alumina/Ag.

- Fig.2: Impedance spectra of the cell with polished surfaces of the solid electrolyte at different temperatures.
- Fig.3: Impedance spectra of the cell with saw-cut surfaces of the solid electrolyte at different temperatures.
- Fig.4: Analogue network for the cell.
- Fig.5: Results of the approximation of the experimental data in Fig.2, 50°C by the network in Fig.4 ( solid curves ).





ļ



Fig.2



のないとうとうない

**1**2223



A CALL CALL OF



•





Fig.5

J.

