

THE SMALL-SIGNAL A.C. RESPONSE OF  $\beta$ -PbF<sub>2</sub>

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The small-signal a.c. response of symmetrical cells with nominally pure or bismuth-doped  $\beta$ -PbF<sub>2</sub> as solid electrolyte and Pt or Au electrodes has been studied at controlled oxygen pressures over the frequency range 10<sup>-4</sup>Hz to 50kHz for temperatures ranging from 25°C to 450°C. The results indicate that oxygen is present as a mobile impurity in  $\beta$ -PbF<sub>2</sub> and in Pb<sub>1-x</sub>Bi<sub>x</sub>F<sub>2+x</sub> and participates in an electrode adsorption-reaction sequence.<sup>2</sup> The data have been interpreted with the aid of three different, but related, equivalent circuits, one involving a constant-phase-angle element, the second a single finite-length Warburg element, and the third two finite-length Warburg elements. Nonlinear-least squares analysis of the complex admittance data yields the dependence of the circuit elements on temperature and oxygen pressure.

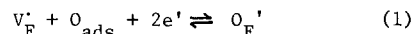
INTRODUCTION

Cubic lead fluoride,  $\beta$ -PbF<sub>2</sub>, and solid solutions based on  $\beta$ -PbF<sub>2</sub> are among the best anion-conducting solid electrolytes identified to date [1,2], and their bulk conductivity parameters have been well characterized [3,5]. Their interfacial processes, in contact with a number of electrode materials, have been investigated by cyclic voltammetry [6] and small-signal a.c. techniques [7-9] and an understanding of these processes is beginning to emerge. At elevated temperatures  $\beta$ -PbF<sub>2</sub> readily reacts with oxygen. The influence of oxygen on small-signal a.c. response has been noted by the present authors in an earlier publication [9].

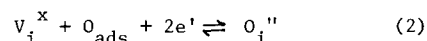
This paper presents a study of the small-signal a.c. response of symmetrical cells of single crystal  $\beta$ -PbF<sub>2</sub> and anion excess solid solutions Pb<sub>1-x</sub>Bi<sub>x</sub>F<sub>2+x</sub> as solid electrolyte and Pt or Au as ionically blocking electrodes. Details of sample preparation and the small-signal a.c. measurement techniques were given in our previous paper [9], together with some representative impedance and admittance plane plots. In the present work we present a more detailed analysis of the data, including the results of some more recent measurements, and further consider the role played by impurity oxygen in the system electrical response.

EQUIVALENT CIRCUITS

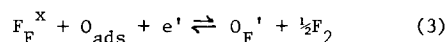
Oxygen may participate in interfacial charge transfer by a number of mechanisms. The reaction



is likely for pure PbF<sub>2</sub>, but the reactions



and or



are perhaps more probable in the extrinsic regions of Pb<sub>1-x</sub>Bi<sub>x</sub>F<sub>2+x</sub>, for which the free mobile fluoride ion vacancy concentration [V<sub>F</sub><sup>'</sup>] is negligible small. For pure PbF<sub>2</sub> transport of oxygen may occur via a vacancy mechanism or through the diffusion of (V<sub>F</sub>O<sub>F</sub>)<sup>x</sup> pairs, while at high temperatures [3,4] an interstitialcy process O<sub>F</sub><sup>'</sup> + F<sub>i</sub><sup>'</sup>  $\rightleftharpoons$  O<sub>i</sub><sup>''</sup> + F<sub>F</sub><sup>x</sup> may occur. The latter process seems reasonable for the anion excess solid solution at all temperatures.

Since the electrodes employed in our measurements were either sputtered or painted onto the

crystals, and therefore somewhat porous in nature, the small-signal a.c. response problem is complicated somewhat by the probable motion of oxygen through the electrode as well as within the electrolyte. An exact theoretical treatment of the small-signal a.c. response of an unsupported system has been published [10] which takes into account the rate limiting diffusion of the product species of an electrode adsorption-reaction sequence into the electrolyte or through a planar electrode. This treatment is applicable in the present case, but only approximately so, as it does not take full account of simultaneous oxygen transport in both the electrolyte and the electrode. For the case of a single mobile intrinsic charge carrying species, and under certain conditions in more general cases, the circuit of Fig. 1 follows this theoretical work.

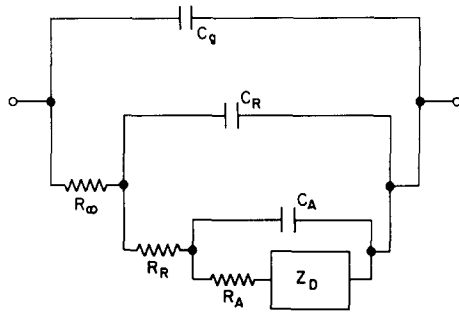


Fig.1. Equivalent circuit with one diffusional impedance

The theoretical treatment [10] yields the following relations for the circuit elements which represent the electrode reaction and adsorption processes:

$$R_R = 2kT/z_p^2 e^2 k_{1f} \quad (4)$$

$$C_A = (R_R k_{1b})^{-1}, \quad (5)$$

$$R_A = R_R k_{1b}/k_{3f} \quad (6)$$

and

$$Z_D = Z_{Do} \frac{\tanh \sqrt{i\omega H^2}}{\sqrt{i\omega H^2}} \quad (7)$$

where the  $k$ 's denote effective rate constants,  $H = \delta/\sqrt{D}$ , where  $\delta$  is a diffusion length, and

$$Z_{Do} = R_R k_{1b} k_{3b} \delta/k_{3f} D. \quad (8)$$

Also included in the circuit of Fig.1 are the geometric capacitance  $C_g$ , the bulk resistivity  $R_\omega$ , and the double layer capacitance  $C_R$ .

Raistrick et. al. [7] have found the frequency-dependent impedance  $Z = A\omega^{-\alpha} - B i\omega^{-\alpha}$  to describe the small-signal a.c. response of the interface between polished  $\beta\text{-PbF}_2$  crystals and

sputtered Pt or Au electrodes in inert ambients. The Kramers-Kronig relation leads to the equation  $B = A \tan(\alpha\pi/2)$  for the coefficients  $A$  and  $B$  in this impedance [7,11]. With this relation one has the constant-phase-angle (CPA) impedance

$$Z_D = K(i\omega)^{-\alpha}. \quad (9)$$

In our data analyses we have employed the equivalent circuit of Fig. 1 with both the finite-length Warburg impedance for  $Z_D$ , as in Eq.(7), and the CPA form, Eq. (9). While the CPA form did give, in many cases, a better fit to the data it must be noted that at low frequencies the impedance curve, in impedance plane plots, turns towards the real axis, a feature not accounted for when the CPA form is used [9].

In order to provide for the possibility of rate limiting oxygen diffusion in both the electrode and the electrolyte, some of the experimental results were analyzed with the equivalent circuit shown in Fig. 2, in which two finite-length Warburg elements appear. The theory underlying this circuit is presented elsewhere [12]. As in the case of the equivalent circuit of Fig. 1, the theoretical treatment provides relationships among the circuit parameters.  $R_R$ ,  $C_A$ , and  $R_A$  have the same form as in Eq. (4)-(6), while  $Z_{D,e}$  and  $Z_{D,c}$  both have form

$$Z_D = Z_{EW} \frac{\tanh \sqrt{i\omega H^2}}{\sqrt{i\omega}} \quad (10)$$

where explicit forms for  $Z_{EW,e}$ ,  $Z_{EW,c}$ ,  $H_e^2$  and  $H_c^2$  are given in Ref. [12].

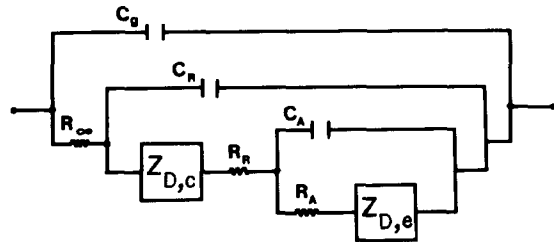


Fig. 2. Equivalent circuit with two diffusional impedances

## RESULTS AND DISCUSSION

Nonlinear least squares fitting results were presented in our previous paper [9] for pure  $\beta\text{-PbF}_2$ . In Table I we present activation enthalpies derived from nonlinear least squares fits of admittance data for extrinsic  $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$  ( $x=0.013$ ) at oxygen pressure

$P_{O_2} = 10$  Pa with sputtered Au and two different painted Pt electrodes to the equivalent circuit of Fig. 1, using the CPA form for  $Z_D$ . As noted in the Table there are discrepancies in some of the fitting parameters obtained from a series of measurements at increasing temperatures and those obtained from a series at decreasing temperatures. It is probable that these arise from a very slowly reversible incorporation of oxygen into the system at higher temperatures.

Table I. Activation enthalpies (eV.) for the circuit elements, Fig. 1, for  $Pb_{1-x}Bi_xF_{2+x}$  ( $x=0.013$ ),  $P_{O_2} = 10$  Pa.

Element	Electrode		
	Au	Pt(1)	Pt(2)
K	0.296	0.223	0.372(i) 0.186(d)
$R_A$	0.378	0.315	0.279
$C_A$	0.216	0.265	
$R_R$	0.493	0.425	0.436
$C_R$	0.262	0.257	
$R_\infty$	0.542(i) 0.531(d)	0.556(i) 0.574(d)	0.548

(i) increasing temperature  
(d) decreasing temperature

If the rate constants  $k_{1b}$  and  $k_{3f}$  in Eqs. (5) and (6) have the conventional Arrhenius form  $k = k_0 \exp(-\Delta H / kT)$ , then plots of  $\log_e R_R$  against  $\log_e R_A$  and  $\log_e C_A$  against  $\log_e R_R$  should be linear. These plots are shown in Figs. (3) and (4) for  $Pb_{1-x}Bi_xF_{2+x}$  ( $x=0.013$ ) with Pt electrodes. The observed slopes of nearly +1 and -1 are to be expected if  $k_{1b}$  and  $k_{3b}$  do not change appreciably over the temperature range involved, a condition roughly consistent with the activation enthalpies of Table I.

Quantitatively we find for Au electrodes:

$$\ln R_R = (1.03 \pm 0.03) \ln R_A - (1.02 \pm 0.23) \quad (11)$$

and

$$\ln C_A = - (0.66 \pm 0.05) \ln R_R - (10.05 \pm 0.37), \quad (12)$$

and for Pt electrodes

$$\ln R_R = (1.04 \pm 0.04) \ln R_A - (1.57 \pm 0.22), \quad (13)$$

$$\ln C_A = - (0.99 \pm 0.06) \ln R_R - (6.90 \pm 0.46), \quad (14)$$

and

$$\ln C_A = - (0.93 \pm 0.07) \ln R_R - (7.61 \pm 0.41), \quad (15)$$

where the last two results were obtained for two different Pt electrodes.

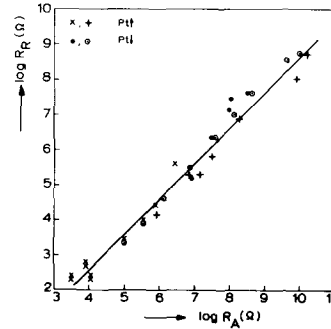


Fig.3. Log -log plot of the equivalent circuit elements  $R_R$  and  $R_A$  for  $Pb_{1-x}Bi_xF_{2+x}$  ( $x=0.013$ ) with Pt electrodes.  $P_{O_2} = 10$  Pa. Data are for increasing ( $x, +$ ) and decreasing ( $\cdot, \odot$ ) temperature.

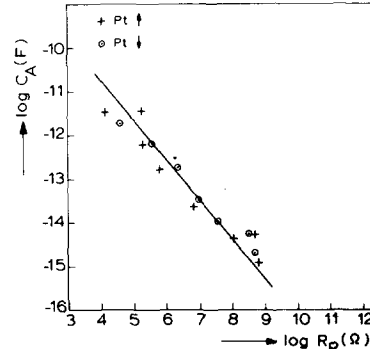


Fig.4. Log -log plot of the equivalent circuit elements  $C_A$  and  $R_R$  for  $Pb_{1-x}Bi_xF_{2+x}$  ( $x=0.013$ ) with Pt electrodes.  $P_{O_2} = 10$  Pa. Data are for increasing ( $x, +$ ) and decreasing ( $\cdot, \odot$ ) temperature.

Nonlinear least squares fits were also made to the equivalent circuit of Fig.2 for one of the  $Pb_{1-x}Bi_xF_{2+x}$  ( $x=0.013$ ) samples with Pt electrodes at  $P_{O_2} = 10$  Pa. The standard deviations

of the fits, calculated from

$$= [N^{-1} \sum_i |(Y_{i,fit} - Y_{i,exp}) / Y_{i,exp}|^2]^{1/2} \quad (16)$$

ranged from 0.04 to 0.07 with an average of 0.05 for five admittance runs over the temperature range from 77°C to 304°C. Although it proved not possible to determine best fit values of the circuit parameters  $R_A$  and  $R_R$ , the fits obtained with these elements set equal to zero were of appreciably better quality than those obtained

Table II. Circuit parameters and standard deviations ( $\sigma$ ) for admittance of Pb<sub>1-x</sub>Bi<sub>x</sub>F<sub>2+x</sub> ( $x=0.013$ ) sample with Pt electrodes at 211°C, fit to equivalent circuit of Fig. 2.

P <sub>O<sub>2</sub></sub> (Pa)	Z <sub>EW,e</sub> (10 <sup>4</sup> Ω)	H <sub>e</sub> <sup>2</sup>	R <sub>A</sub> (10 <sup>3</sup> Ω)	C <sub>A</sub> (10 <sup>-4</sup> F)	Z <sub>EW,c</sub> (10 <sup>3</sup> Ω)	R <sub>R</sub> (10Ω)	C <sub>R</sub> (10 <sup>-7</sup> Ω)	R <sub>∞</sub> (10 <sup>2</sup> Ω)	C <sub>g</sub> (10 <sup>-10</sup> F)	σ
1.46	2.15	490	1.80	1.25	4.20	6.00	0.99	4.41	2.41	0.03
10.	1.62	420	2.48	1.20	4.54	5.76	1.28	4.72	2.43	0.02
187.	1.15	280	1.53	1.43	4.99	5.67	1.05	4.73	2.43	0.04
1623.	1.01	360	1.14	1.47	5.20	6.12	1.09	4.76	2.43	0.03

with the equivalent circuit of Fig. 1 with either the CPA or finite-length Warburg form for Z<sub>D</sub>.

The activation enthalpies obtained for the circuit parameters Z<sub>EW,e</sub>, H<sub>e</sub><sup>2</sup>, C<sub>A</sub>, Z<sub>EW,c</sub>, C<sub>R</sub> and R<sub>∞</sub> are respectively 0.338, -0.047, 0.240, 0.351, 0.322, 0.588 eV. Although it was possible to determine a value of H<sub>e</sub><sup>2</sup> for each data set, the data did not extend to low enough frequencies to permit a determination of H<sub>c</sub><sup>2</sup>, and the values obtained for H<sub>e</sub><sup>2</sup> and its activation enthalpy must be considered somewhat uncertain.

Table II presents the least-squares fitting results for the same electrode/electrolyte combination at 211°C for four different values of oxygen partial pressure. For these, more recent, measurements the frequency range was 10<sup>-2</sup>Hz to 1MHz, and it proved possible to simultaneously determine nine circuit parameters, although the values for H<sub>e</sub><sup>2</sup> must be considered quite approximate. The circuit parameters Z<sub>EW,e</sub>, C<sub>A</sub>, and Z<sub>EW,c</sub> are seen to vary monotonically with oxygen partial pressure while the other parameters, with the exception of R<sub>A</sub> and H<sub>e</sub><sup>2</sup> are nearly constant. These results and the small standard deviations of the fits suggest that the equivalent circuit employed here provides a good description of the processes determining the small-signal characteristics of this system.

#### ACKNOWLEDGEMENTS

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