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*Decomposition voltage for the electrolysis of alumina at low temperatures**

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The apparent decomposition voltage for the electrolysis of alumina in an equimolar Na_3AlF_6–Li_3AlF_6 electrolyte was measured over a temperature range of 800 to 1000° C by the extrapolation of voltage-current plots to zero current. Temperature coefficients of -1.9 and $-2.4\,mV\,^\circ C^{-1}$ were determined for conditions of variable alumina activity (constant concentration) and unit activity (saturated), respectively. The overvoltage contribution to the temperature dependency was estimated to be about $-1.6\,mV\,^\circ C^{-1}$ (versus a $-0.6\,mV\,^\circ C^{-1}$ dependency for the reversible decomposition voltage). Reduced alumina solubility at low temperatures also appeared to increase the overvoltage, but was of secondary importance.

1. Introduction

For many years there has been an interest in reducing the temperature for electrolysis of alumina from the 970° C level used typically in commercial reduction cells. (The use of relatively low melting point electrolytes was disclosed in Hall's original patents, one of them [1] containing the statement: '. . . a low red heat is sufficient for carrying on the process'.) Potential advantages of lower temperature include increased current efficiency, lower carbon consumption and longer cell life. However, these advantages must be balanced against higher electrolyte resistivity and lower solubility and dissolution rate for alumina [2]. It is also likely that low electrolysis temperatures adversely affect the decomposition voltage for the predominant overall cell reaction

$$2Al_2O_3 + 3C \rightarrow 3CO_2 + 4Al. \qquad (1)$$

In the absence of conventional nomenclature, the decomposition voltage will be defined as the absolute value of the reversible cell voltage plus overvoltage, i.e.

$$E_d = |E_r| + \eta. \qquad (2)$$

The reversible component is given by

$$E_r = \frac{-\Delta G^0}{6F} + \frac{RT}{6F}\ln a_{Al_2O_3}, \qquad (3)$$

where ΔG^0 is the standard free energy change for Reaction 1, F is Faraday's constant (96 490 C mole^{-1}), R is the gas constant (8.314 J mole^{-1} K^{-1}), T is the absolute temperature, and $a_{Al_2O_3}$ is the activity of alumina (all other reactants are assumed to be at unit activity). The standard free energy term is calculated as [3]

$$\Delta G^0/6F = 1.897 - 5.6 \times 10^{-4}T \qquad (4)$$

and the alumina activity may be related to concentration, C, by [4]

$$a_{Al_2O_3} = \left(\frac{C}{C_s}\right)^{2.77} \qquad (5)$$

where C_s is the alumina concentration at saturation. Equation 2 now becomes

$$E_d = 1.897 - 5.6 \times 10^{-4}T - 0.40 \times 10^{-4}\,T\ln\frac{C}{C_s} + \eta. \qquad (6)$$

The overvoltage component in commercial reduction cells operating at 970° C is about 0.6 V. Most of this occurs at the anode, and is usually ascribed to a reaction or charge transfer process.

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Cathode overvoltage is generally thought to be minimal, and if present is due to ionic diffusion effects.

Although the temperature dependency of E_r can be determined from Equations 3 and 4, the effect of temperature on the overvoltage contribution to E_d is somewhat uncertain. Since overvoltage is associated with thermally activated processes, it should decrease with increasing temperature. Kinetic arguments lead to expressions of the form [5]

$$\left(\frac{\partial\eta}{\partial T}\right)_I = \frac{n\alpha F\eta - \Delta H^*}{n\alpha FT} \tag{7}$$

where n is the number of electrons involved in the rate determining step of the electrode reaction, α is the fraction of the overvoltage assisting in the overall direction of the reaction, ΔH^* is the heat of activation at the reversible potential and I is current.

Richards and Welch [6, 7] measured anode overvoltage dependencies ($\partial\eta/\partial T$) of up to -1.5 mV ° C^{-1} for alumina electrolysis over the temperature range 950 to 1050° C. Haupin [8], on the other hand, found temperature to have an insignificant effect on overvoltage at 970–1010° C for normal current densities. A number of early investigators measured decomposition voltages at various temperatures near and above 1000° C. Thompson and Seyl [9] showed a -1.6 mV° C^{-1} dependency over a temperature range of 960–1230° C for cryolite melts containing 9.5–18.5% Al_2O_3. Cuthbertson and Waddington [10] observed a large temperature effect (-5 mV ° C^{-1}) in cryolite–16% Al_2O_3 at 975–1045° C, and suggested that the values at the lower temperatures may have been influenced (increased) by incomplete dissolution of alumina. Drossbach [11] also measured a large temperature dependency (-6.5 mV ° C^{-1}) in a 65% sodium cryolite–30% lithium cryolite–5% alumina bath at 910–950° C. However, his results were inconsistent under varying electrolysis conditions. Temperature effects bracketing Thompson and Seyl's value were obtained by Tverdovski and Molchanov [12] at 965–1000° C: -2.3 mV ° C^{-1} in cryolite–10% Al_2O_3, and -1.4 mV ° C^{-1} in cryolite–20% Al_2O_3.

To determine the effect of lowering the electrolysis temperature below 900° C, decomposition voltages were measured over the range 800 to 1000° C using an equimolar Na_3AlF_6–Li_3AlF_6 solvent. This salt composition has a fusion temperature of about 780° C [13], good electrical conductivity at low temperatures [14], and has been reported to have a reasonable alumina solubility ($\simeq$ 2 wt%) at 800° C [15, 16].

2. Procedures and results

The electrolysis tests were conducted in a graphite crucible that contained a 1 cm i.d. insulating sleeve of either alumina or boron nitride (Fig. 1). The alumina sleeve resulted in a variable Al_2O_3 concentration approaching saturation ($a_{Al_2O_3} \simeq 1$), whereas the boron nitride sleeve allowed tests to be conducted at a relatively constant Al_2O_3 level ($a_{Al_2O_3} \leqslant 1$ and variable). The anode was a 0.65 cm diameter spectrographic grade graphite rod. Voltage–current (V–I) data were generated by reducing the electrolysis current (provided by a Hewlett-Packard 6224B power supply) incrementally from about 1.4 A. Decomposition voltages were estimated by linear extrapolation of V–I

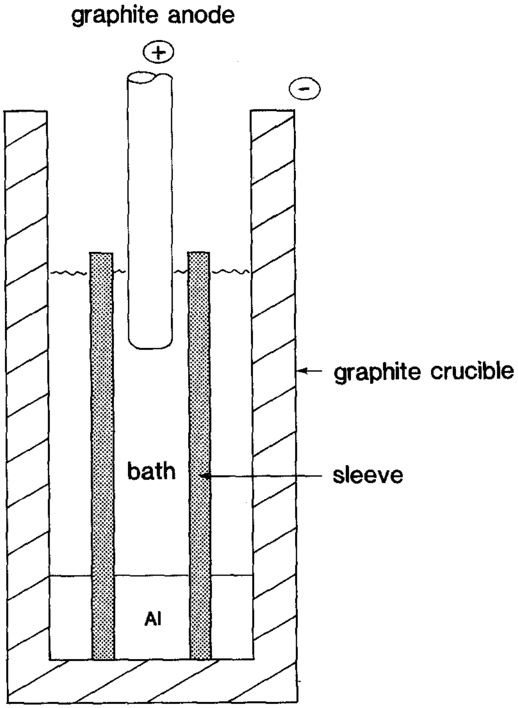

Fig. 1. Cell used for electrolysis tests. Insulating sleeve was either alumina or boron nitride.

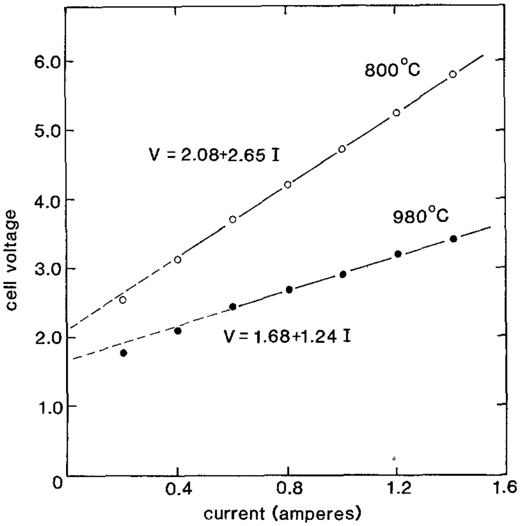

Fig. 2. *V–I* plots for electrolysis of alumina in equimolar Na_3AlF_6–Li_3AlF_6 solvent at 800 and 980° C. Cell contained an alumina sleeve.

plots to zero current. Although this extrapolated (apparent) decomposition voltage has no well-defined theoretical significance, it has a use in the operation and economics of practical electrolytic processes.

Typical *V–I* plots at 800 and 980° C are shown in Fig. 2 for tests conducted with an alumina sleeve. The plots were linear above 0.4 A, allowing good estimates of the decomposition voltages to be made. It is apparent from Fig. 2 that the decomposition voltage at 800° C is about 400 mV higher than that at 980° C. Figure 3 shows decomposition voltages that were extrapolated from *V–I* data (currents of 0.4 to 1 A) obtained over the entire temperature range. There was good agreement among three separate runs (giving an average temperature dependency of -2.4 mV° C^{-1}), and no significant 'hysteresis' effect was evident, i.e. the same results were obtained upon heating and cooling. It is also noteworthy that the decomposition voltage at 970° C is about equal to that typically measured in commercial cells ($\simeq 1.7$ V).

Figure 4 gives the results for tests conducted with a boron nitride sleeve. The data show a somewhat smaller temperature dependency than obtained with the alumina sleeve (-1.9 mV° C^{-1}). Electrolyte samples taken before and after the test contained 4.4 and 4.2 wt% Al_2O_3, respectively. With both sleeve materials, the absolute decomposition voltages were slightly dependent on the current range used for extrapolation (lower E_d values for lower currents, as expected), but the temperature dependency remained fairly constant.

3. Disucussion

A temperature coefficient of -2.4 mV° C^{-1} as

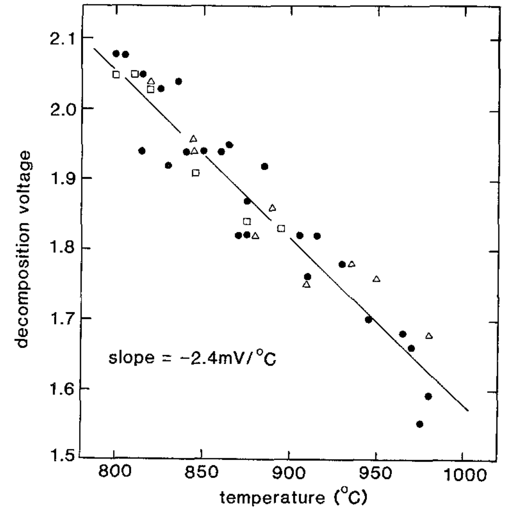

Fig. 3. Effect of temperature on apparent decomposition voltage for electrolysis of alumina in equimolar Na_3AlF_6–Li_3AlF_6 solvent. Cell contained an alumina sleeve. Current interval for extrapolation: 0.4–1.0 A. Different symbols indicate three separate runs.

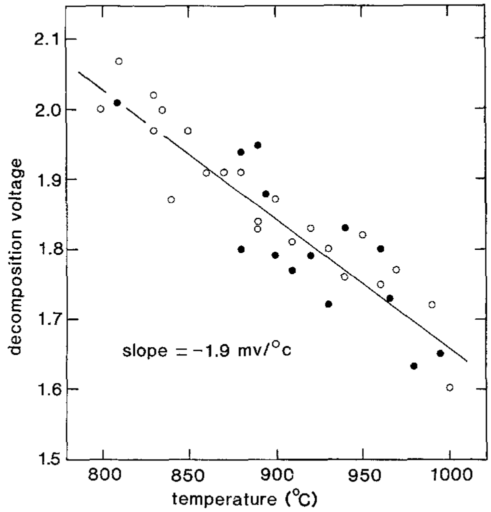

Fig. 4. Decomposition voltage versus temperature for alumina electrolysis in a cell containing a boron nitride sleeve. Current interval for extrapolation: 0.4–1.0 A. Solid symbols, heating cycle; open symbols, cooling cycle.

obtained with the alumina sleeve is considerably greater than that predicted on the basis of reversible electrode reactions (− 0.56 mV ° C^{-1} when $a_{Al_2O_3} = 1$). There must, therefore, be a rather large effect of temperature on overvoltage, namely about −1.8 mV ° C^{-1}. In addition to the effect of temperature *per se* on overvoltage, variations in alumina concentration could affect the observed decomposition voltage because of reduced solubility at the lower temperatures. Published data are inconsistent, but it appears that anode overvoltage increases with decreasing alumina content, especially at levels below about 4 wt% [17]. This is in agreement with the results obtained using the boron nitride sleeve, which showed a smaller dependency of E_d on temperature (− 1.9 mV ° C^{-1}). Allowance should be made in the latter case, however, for the variable alumina activity. Setting $C/C_s \simeq 0.5$ at 1000° C and $a_{Al_2O_3} \simeq 1$ at 850° C (saturation) gives a contribution of about + 0.25 mV ° C^{-1} to the temperature dependency of E_d, i.e. E_d at 1000° C is increased by 35 mV because of the ln C/C_s term in Equation 6. The actual difference between the temperature coefficients for the two tests is, therefore, only 0.2–0.3 mV ° C^{-1}. This indicates that the effect of reduced alumina solubility on the decomposition voltage at low temperature is minimal; the effect of temperature *per se* on overvoltage is the most important factor influencing the temperature dependency of the decomposition voltage.

The magnitude of $\partial\eta/\partial T$ appears to be about − 1.6 mV ° C^{-1}, i.e. − 1.9 mV ° C^{-1} (BN sleeve test) + 0.25 mV ° C^{-1} (ln $a_{Al_2O_3}$ term) − 0.56 mV ° C^{-1} (temperature dependence of $\Delta G^0/6F$). This value is consistent with the aforementioned measurements of Richards and Welsh on anode overvoltage in which temperature coefficients as large as − 1.5 mV ° C^{-1} were observed. Although it is possible that the cathodic overvoltage could also be increased at low temperature [18], especially in a small electrolysis cell where stirring effects are negligible, we note that similar results have been obtained in nominal 100 A tests and in 15 kA pilot cell studies utilizing commercial carbon anodes and wetted TiB_2 cathodes [19].

In summary, reducing the electrolysis temperature for alumina has the disadvantage of increasing the decomposition voltage to a considerably greater extent than would be predicted on the basis of reversible electrode reactions. The greatest factor in this increase appears to be due to the effect of temperature, *per se*, on overvoltage (≃ − 1.6 mV ° C^{-1}). Reduced alumina solubility also contributes to the increased overvoltage, but is a secondary factor. With regard to commercial electrolysis at, say, 850° C, the combined effects of temperature and reduced alumina solubility result in a decomposition voltage penalty of about 0.3 V, which at 90% current efficiency represents a specific energy increase of 1 kWh per kg of aluminium produced.

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