

Decomposition of β -alumina in an oxygen potential gradient

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Received 15 September 1982

Single phase sodium β -alumina solid electrolyte was found to undergo isothermal phase separation in electrochemical cells, where a large oxygen potential gradient was imposed across the electrolyte and electrodes, not reversible to sodium ions, were short circuited. The experimental conditions and evidence of decomposition are outlined and a thermodynamic explanation for the phenomenon is given. This finding may lead to new methods for making multi-layered ceramic materials involving ionic conductors.

1. Introduction

During the course of electrochemical studies on β -alumina solid electrolytes, it was accidentally found that they undergo isothermal phase separation in oxygen potential gradients under closed circuit conditions. This phenomenon has not been reported in the literature. The new experimental findings and a possible explanation are the subject of this paper. The observation has relevance to a number of potential applications of β -alumina and related solid electrolytes, when electrodes are not reversible to the migrating ion. It also points to new methods of making layered ceramic materials involving ionic conductors.

2. Experimental observation

An oxygen potential difference was maintained by passing pure oxygen inside and a CO + CO₂ gas mixture outside a closed end β -alumina tube, as shown in Fig. 1. The ratio of CO to CO₂ in the gas mixture was 1.42. The flow rate of oxygen was 1.5 cm³ s⁻¹, and of the CO + CO₂ mixture was 5 cm³ s⁻¹. The solid electrolyte tube was prepared by slip casting and subsequent sintering. Microstructural examination showed that the solid electrolyte was homogeneous without second phase precipitates. The flat-closed-end of the tube was platinized both inside and outside. Porous platinum sheets, spot welded to platinum wires, were spring loaded against the platinized surfaces. The cell was held at 1173 K for 2 h with the platinum leads joined together outside the

furnace. After cooling to room temperature, the cell was dismantled and the solid electrolyte was sectioned vertically. Metallographic examination of the section showed the formation of new phases on both platinized surfaces. The inside surface exposed to oxygen had developed a layer of NaAlO₂, whereas the outside surface exposed to the CO + CO₂ gas mixture was essentially pure alumina. A microprobe trace of sodium concentration across the section is shown in Fig. 2. The presence of NaAlO₂ and Al₂O₃ on the outside surfaces was also confirmed by X-ray diffraction. The experiment thus provides clear evidence for the net transport of Na₂O from the low oxygen potential region to the high oxygen potential side at constant temperature and under short circuit conditions. The decomposition of β -alumina into pure Al₂O₃ on one side and NaAlO₂ on the other is remarkable. It is important to note that the oxygen partial pressures on both sides of the solid electrolyte were many orders of magnitude higher than the decomposition pressure of β -alumina.

3. Explanation

The experimental observation outlined above raises a number of fundamental questions. What is the driving force for the isothermal decomposition of stable β -alumina in an oxygen potential gradient? Can the decomposition occur under open circuit conditions? Is there a threshold oxygen potential difference below which decomposition will not occur? Some general answers to these questions can be formulated.

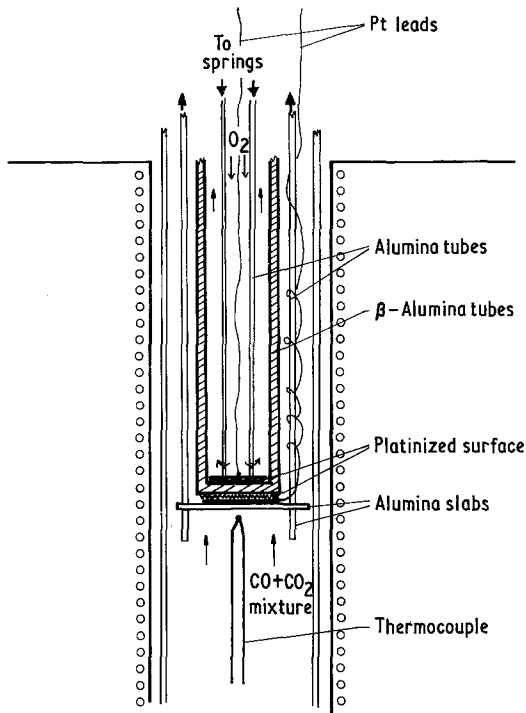
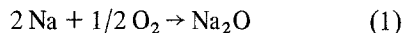


Fig. 1. Schematic diagram of the apparatus.

Since the solid electrolyte was homogeneous, the activity of Na_2O may be assumed to be the same on both sides of the electrolyte at the beginning of the experiment. When different oxygen potentials are established by the gas phase on each side, a gradient in sodium activity across the electrolyte results by virtue of the equilibria:



$$K = a_{\text{Na}_2\text{O}} / (a_{\text{Na}}^2 \cdot P_{\text{O}_2}^{1/2}) \quad (2)$$

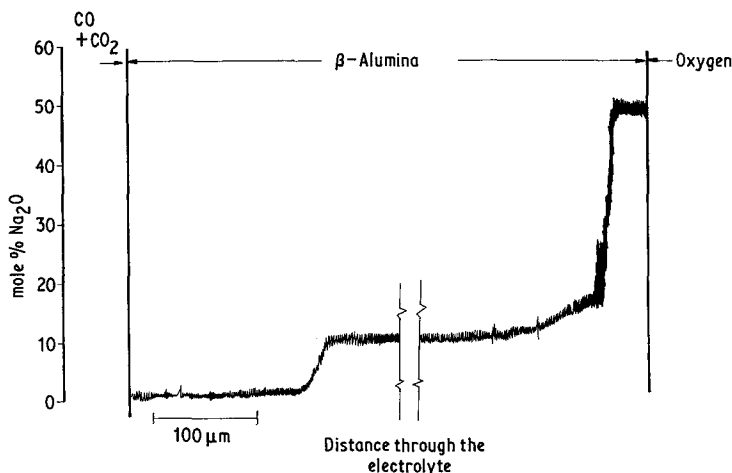
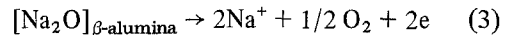


Fig. 2. Variation of sodium concentration across the electrolyte after the experiment.

The sodium ions will try to migrate from the lower oxygen potential side to the higher oxygen potential electrode. Since β -alumina is a predominantly ionic conductor, the requirement of charge compensation would limit sodium transport under open circuit conditions. When the leads are short circuited, there is no hindrance to the flow of sodium ions. In the absence of electrodes reversible to sodium, sodium ions can only be generated or consumed by the reaction,



resulting in net transport of Na_2O from the low to the high oxygen potential electrode. Because of the large nonstoichiometric range of β -alumina, the transport of Na_2O will initially result in a change of composition of the β -phase at the two electrodes. This compositional change will decrease the activity of Na_2O at the low oxygen potential side. There will be a corresponding increase in the activity of Na_2O at the high oxygen potential side. These changes in the activity of Na_2O will reduce the initial gradient in the activity of sodium, and hence the driving force for sodium transport. If the initial difference in the activity of sodium can be completely neutralized by changes in composition of β -alumina (and therefore in the activity of Na_2O), new phases will not form.

The variation of the activity of Na_2O with composition in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ system at 1173 K [1] is shown in Fig. 3. The activity variation within the β -phase fields is not accurately known. The maximum possible variation in $\log a_{\text{Na}_2\text{O}}$ within the β -phases is 4.96 at 1173 K. From this infor-

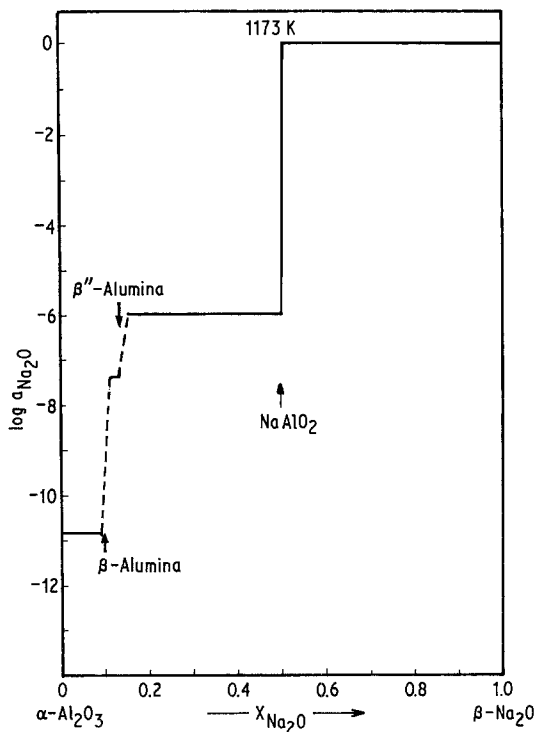
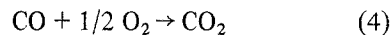


Fig. 3. Variation of the activity of Na_2O with composition in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ system at 1173 K [1].

mation it can be estimated that a difference in oxygen potential, $\Delta\mu_{\text{O}_2} = RT \ln (P'_{\text{O}_2}/P''_{\text{O}_2})$, greater than $216.5 \text{ kJ mol}^{-1}$ will lead to the decomposition of β -alumina to α -alumina on one side and NaAlO_2 on the other at 1173 K. For smaller oxygen potential differences between the electrodes the following situations may be visualized depending on the initial composition of the β -phase and the magnitude of the oxygen potential difference: (a) changes in composition of the β -phase at each electrode, (b) precipitation of α -alumina on one side and increase in concentration of Na_2O in the β -phase on the opposite side, (c) precipitation of NaAlO_2 on one side and decrease in the concentration of Na_2O in β -phase on the other side, or (d) precipitation of both α -alumina and NaAlO_2 at the two electrodes. Assuming that chemical equilibrium is attained in the gas phase near the platinum electrodes, the oxygen potential difference between the electrodes during the experiment may be evaluated as $368.2 \text{ kJ mol}^{-1}$. The oxygen potential established by the $\text{CO} + \text{CO}_2$ mixture is calculated from thermodynamic data [2] and gas composition;



$$\mu_{\text{O}_2} = RT \ln P_{\text{O}_2} = 2 \Delta G_4^\circ + 2RT \ln (P_{\text{CO}_2}/P_{\text{CO}}) \quad (5)$$

When equilibrium is attained any trace oxygen molecules originally in the gas mixture would be consumed by reaction with CO. This oxidation reaction will not significantly affect the CO_2/CO ratio in the mixture. Thus the low oxygen potential established by the gas mixture is not influenced by the small number of oxygen molecules that may be present initially in the gas phase. The large oxygen potential difference between electrodes provides sufficient driving force for decomposition at each electrode. The experimental result agrees with this deduction. For a more quantitative analysis precise information on the defect chemistry of the β -phase and characterization of decomposition products as a function of oxygen potential difference and initial composition of β -alumina are required.

4. Applications

The experimental observation of isothermal phase decomposition in an oxygen potential gradient has obvious consequences in a number of device applications of β -alumina. This phenomenon can cause problems when the exchange of sodium between the electrodes and the electrolyte is prevented either by blocking electrodes or severe polarization effects. Incipient phase decomposition under such conditions may also be associated with crack initiation.

The results of this study also point to a convenient method for making layered ceramic structures involving ionic conductors by placing an initially homogeneous composition in an oxygen potential gradient with surfaces short circuited by a metallic conductor. Perhaps an alternative method of manufacture would be solid state electrolysis of ionic conductors with inert electrodes. The full potential of these ideas can only be assessed by more detailed experimental studies.

Acknowledgement

The author wishes to thank the Natural Sciences and Engineering Research Council of Canada for financial support.

References

- [1] K. T. Jacob and O. M. Sreedharan, unpublished research.
- [2] D. R. Stull and H. Prophet et al., JANAF Thermochemical Tables, NSRDS-NBS 37, US Department of Commerce, Washington, DC, USA.