

Preliminary Note

A Room Temperature β -Alumina Primary Cell Employing Sodium/Potassium Alloy as Anodic Reactant

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Introduction

The renewed interest in solid electrolytes arising from the discovery of high ionic mobility and negligible electronic conductivity in Ag_4RbI_5 (Ag^+ mobile) [1, 2] and the non-stoichiometric $\text{Na}_2\text{O} \cdot \kappa \text{Al}_2\text{O}_3$ (Na^+ mobile) [3 - 5] has prompted investigations into the possible development of solid state electrochemical cells; such cells would have an advantage over conventional aqueous systems in the areas of shelf-life, miniaturization and geometrical flexibility. In the particular case of the " β -alumina" family ($5 < \kappa < 11$) a high open circuit voltage is possible since these compounds may be coupled with sodium ($E_0[\text{Na}/\text{Na}^+] = 2.714 \text{ V vs. H}_2/\text{H}^+$ [6], whose reactivity towards water has precluded its utilization in aqueous systems, as the anode material.

In order to prevent building up of a highly resistive discharge product at the cathode/electrolyte interface it is necessary either to employ a solid cathodic material in which the anodic product may disperse or, less preferably, to use a moisture free non-aqueous solvent (the β -alumina compounds are moisture sensitive) in which it is soluble.

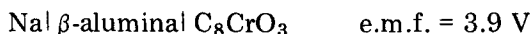
A solid cathode, in order to function efficiently, must have the ability to accept alkali metal cations into its structure without undergoing a phase change. Here the ionic lattice must present a fixed skeletal structure which can act as host to the injected alkali cations. To function in this way the

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structure must have either tunnels through which the cations can migrate or sandwich layers in whose plane the cations are mobile, metal ions in high oxidation states capable of ready reduction to lower oxidation states, considerable covalent bonding character in the solid matrix and a suitable electronic band structure to allow the necessary delocalization of negative charge acquired by the lattice during discharge.

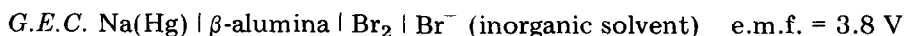
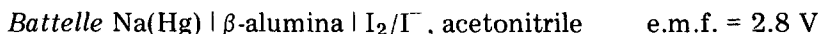
When the ion, such as Na^+ , is incorporated into sandwich layers the process of injection is known as intercalation, and to date this would appear to be the most important type of incorporation. A well characterized instance of this is MoO_3 [7, 8], where the discharge process may be regarded as the formation of molybdenum bronzes Li_xMoO_3 due to intercalation of lithium ions into the van der Waals layers of the antifluorite structure. A further example where intercalation is known to occur readily is TiS_2 [9] which has the CdI_2 structure.

Two further problems relating to solid state electrochemical cells are the difficulty of establishing good initial electrical contact at the solid anode/solid electrolyte interface and the loss of contact which usually arises during discharge due to the "dissolution" of the anode. This would be true for the ambient temperature system proposed by Armand [10]:



for which no extended discharge data are presented.

Attempts to overcome this disadvantage have involved the use of sodium amalgam, as in the cells proposed by General Electric (U.S.A.) [11] and Battelle (Geneva) [12]:



but here, especially in the case of a primary cell, only a partial solution is presented since the realisable capacity is limited by an amalgam composition of ~2% sodium, above which the alloy is entirely solid at room temperature (20 °C).

With a view to overcoming this limitation it was decided to investigate the possible use of Na(K) alloys in conjunction with β -alumina. The Na/K system is either completely liquid or two-phase at room temperature over the entire composition range.

Experimental

In the present cell a cathode composed of a compound of CrO_3 and graphite was employed since this material is known to be electrochemically active in the organic electrolyte necessary as contact medium with the ceramic [19].

Preparation

The chromium trioxide intercalate of graphite was prepared by grinding natural graphite powder (Hopkin and Williams Ltd. 98 - 99% pure) using an agate pestle and mortar, and then sieving to obtain material of grain size less than $152\ \mu\text{m}$. 12 g of this powder were then suspended in a solution of 60 g of CrO_3 (Hopkin and Williams Analar) in $400\ \text{cm}^3$ of Analar glacial acetic acid (BDH Ltd.) and refluxed for 10 min with gentle stirring. After cooling, the reaction product was filtered and washed with glacial acetic acid — to remove unreacted CrO_3 — until the filtrate was colourless. The intercalate was then oven dried at $100\ ^\circ\text{C}$ to constant weight and stored under these conditions. The composition of material prepared in this fashion ranged from $\text{C}_{13.7}\text{CrO}_3$ to $\text{C}_{14.3}\text{CrO}_3$, calculated from the gain in weight. Examination by X-ray diffraction confirmed incorporation of CrO_3 into the graphite lattice, the d -spacings obtained being in reasonable agreement with those reported in the literature [13].

Preparation and handling of sodium/potassium alloy

The alloy was prepared and handled in a glove-box under dry argon (BOC Ltd., H. P. Grade). A high purity inert atmosphere processing plant designed and manufactured by Lintott Eng. Ltd. was employed. Both the potassium (H & W lump in liquid paraffin) and sodium (BDH pellets in liquid paraffin) were melted under liquid paraffin in porcelain dishes placed on a hot-plate, and the molten potassium kneaded into the sodium gradually over a period of 20 min to produce an alloy composition of 45 atom%Na, 55 atom%K. After cooling to room temperature the alloy was washed free of liquid paraffin by means of petroleum ether, which was allowed to evaporate before use. The surface of the alloy remained bright for up to half an hour inside the glove-box.

Cell assembly and design

The cell employed in the investigation is shown in Fig. 1. Assembly and electrical testing of the cell were conducted as a single series of operations without admitting air to the glove-box. The β'' -alumina tube (overall height 17.25 cm, outside diameter 1.25 cm.) was first inserted into the Pyrex boiling tube, which was then filled with intercalate which had been wetted with a molar solution of LiClO_4 in propylene carbonate to act simply as a contact medium onto the ceramic. The organic electrolyte was dried over molecular sieve prior to use. The alloy was then finally poured into the ceramic tube and the platinum leads inserted. The level of intercalate outside and that of the alloy inside were each $\sim 2\ \text{cm}$ below the top of the ceramic tube.

Techniques

Electrical measurements on cells

Various resistors were placed across the terminals of the cell (special hermetically sealed leads connected the cell inside the glove-box to the

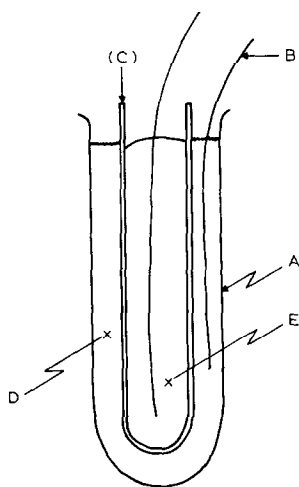


Fig. 1. Experimental cell. A, Pyrex boiling tube; B, Pt leads; C, ceramic separator; D, CyCrO_3 /organic electrolyte; E, Na/K alloy.

resistors outside) and the potential difference measured to obtain polarization data.

For extended discharge, the p.d. was monitored as a linear function of time on a Servoscribe potentiometric recorder type R.E.511.20. A Marconi Instruments universal bridge TF1313A was used for the impedance measurements.

All measurements were obtained at $20 (\pm 2)^\circ\text{C}$.

X-ray photoelectron spectroscopic studies on the ceramic electrolyte

X.P.S. studies were performed on ceramic material taken from cells which had been subjected to extended discharge to determine the nature of the mobile species present. Previous studies by X.P.S. have been made on solid electrolytes [14]. The relative percentages of the mobile species in the β -aluminas may be estimated approximately from the intensities of the photoelectron peaks.

The sodium/potassium alloy was removed from the ceramic tube by addition of amyl alcohol in the glove-box. The tube was crushed, washed with methylated spirits and dried, then mounted with double-sided Sello-tape onto the copper block of the standard insertion lock of the AEI ES200B electron spectrometer. The latter incorporated a magnesium K_{α_1, α_2} X-ray source and was operated in the FRR mode with the analyzer entrance and exit slits set at 0.305 cm.

Samples were maintained at 10°C and a pressure of 10^{-7} Torr during a given analysis. The binding energies of the photoelectron peaks were determined with respect to the carbon 1s electron peak at 284.6 eV. This carbon peak results from hydrocarbon contamination of the sample due to pump oil from the vacuum system.

The chromium trioxide intercalate in graphite was also examined by X.P.S.

The chromium 3p, carbon 1s and oxygen 1s electron regions of the chromium trioxide intercalate were recorded. The chromium 3p region showed two separate peaks at binding energies of 48.0 eV and 44.5 eV, in the proportion 3:1. The oxygen 1s electron region was indicative of at least two oxygen species and the total spectrum could be resolved into two peaks with binding energies of 532.4 and 531.0 eV.

Results and Discussion

Electrical tests on cells

The open circuit voltage of the cell at room temperature (20 °C) was found to be 3.75 V and the p.d. on 10 k Ω to be 2.60 V for a nominal cathode composition C₁₄CrO₃.

Figure 2 clearly shows the polarization of the cell to be ohmic in character over the current range studied; the d.c. resistance calculated from this polarization data was 3.13 k Ω , equal within experimental error to that determined by a.c. resistance measurements at 10 kHz, but higher than that which would be expected solely from the ceramic; the resistivity of the latter was found to be 150 Ω cm at 20 °C and 10 kHz using evaporated Au/Au foil contacts, leading to an estimated ohmic contribution to the cell resistance of \sim 825 Ω , assuming an average contact area of 55 cm². An anomaly of this magnitude cannot reasonably be accredited to the ohmic contribution from the cathode. Although a substantial contribution from the ceramic/organic electrolyte interface might be expected [22], the linearity of the cell polarization characteristic over the current density range studied

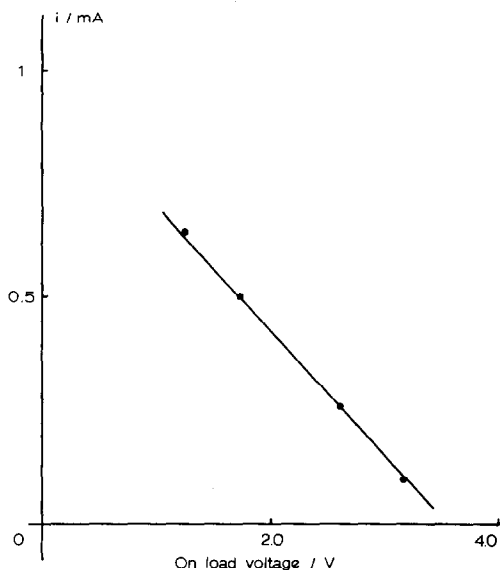


Fig. 2. Polarization characteristic of Na-K/ β -alumina/CyCrO₃ cell.

indicates that the discrepancy must result primarily from non-wetting of the ceramic surface by the liquid Na/K alloy. It has been shown [17], that the degree to which liquid sodium "wets" β'' -alumina is dependent not only on temperature but also on surface roughness of the ceramic, and on the basis of these results [17] it might be expected that unpolished β'' -alumina, such as that used in the present experiments, would not allow appreciable contact with the liquid Na/K alloy, thus giving rise to a high measured impedance.

The internal resistance remained virtually constant throughout the discharge period of six weeks over which the cells were subjected to a constant load of 10 k Ω , resulting in an essentially constant on-load voltage as shown in Fig. 3. On 1 k Ω load, disruption of the ceramic occurred after

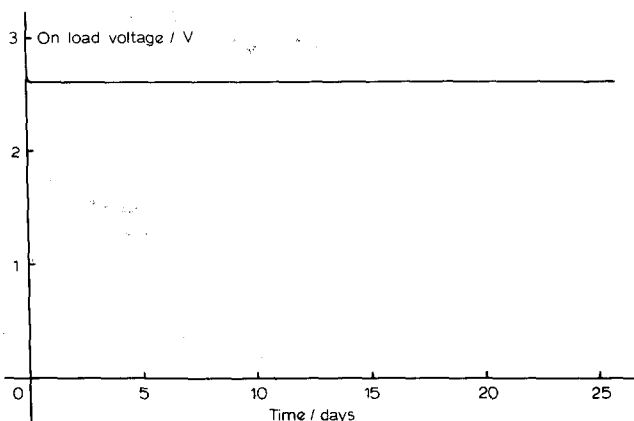


Fig. 3. Discharge characteristic on 10 k Ω load at 20 °C.

approximately one week, characterized by irregular oscillation of the on-load voltage and gas evolution from the cathode compartment due to reaction of the anode with the organic solvent. On removal from the cell the ceramic tube was found to be intact, but its surface presented an extensive and completely random pattern of fine cracks; these were an intense blue colour and the entire body of the ceramic had a bluish tinge indicating the presence of alkali metal [15, 16, 18].

X-ray photoelectron spectroscopic studies of the electrolyte

It was suspected that "break-down" of the ceramic had resulted from penetration by K⁺ causing non-isotropic expansion of the β'' -alumina grains ($c = 22.530$ Å for Na⁺ β -alumina and $c = 22.729$ Å for K⁺ β -alumina [16]) and hence cracking of the ceramic. The presence of potassium and sodium was confirmed by examination of the potassium 2p and sodium 2s electron regions. Both elements were detectable, and the binding energies of the various peaks are presented in Table I. The peak widths at half-height suggested that only one 2p electron doublet was present in the case of potassium and only one 2s electron peak in the case of sodium. The relative peak areas (average of two determinations) enabled an approximate value for

TABLE I

Sample	Spectrum	Binding energy (eV)*		Ref.
Na- β' -alumina	Na 2s	64.2		14
Na/K- β' -alumina	Na 2s	64.2		this work
	K 2p ^{3/2}	303.5	303.3	
		303.15		

*w.r.t. C 1s electron = 284.6 eV.

the relative proportions of the species to be determined; using the relative intensities of the elements values of 20% potassium and 80% sodium were estimated. The binding energy of 62.4 eV for the sodium peak corresponded to that for sodium β' -alumina [14]; no other peaks due to sodium were detected although in earlier work [14] on partially substituted β -aluminas more than one peak was present possibly due to the sodium ions being trapped at intermediate sites in the lattice.

X-ray photoelectron spectroscopic studies on the chromium trioxide-graphite intercalate

The spectra indicate the presence of two distinct chromium species which, on the basis of a previous comprehensive study of chromium oxides and the reduction products of Cr^{VI} at a gold electrode [20], may be assigned to Cr^{III} and Cr^{VI}. The two peaks may be due to a mixture of CrO₃ and Cr(OH)₃ or may reflect a true chromium chromate or a mixture of all three. These results suggest that the compound is not a true intercalate but that reduction of Cr^{VI} occurs, in contradiction to the findings of Ebert *et al.* [21].

Conclusions

It has been shown that the cell as described can supply useful power (~0.6 mW for the experimental cell) suitable for miniature electronic devices such as heart pacemakers, watches and hearing aids. Since non-wetting of the ceramic appears to be a problem, it might be anticipated that polishing of the ceramic surface to reduce the surface roughness factor would lead to increased power capability [17].

The X.P.S. results confirm that potassium penetration of the ceramic occurs and this probably causes the "breakdown" of the ceramic electrolyte. The tendency to "breakdown" appears to be influenced by the discharge rate of the cell and it is possible that for a given internal construction a threshold rate may exist below which breakdown will not occur, although further work would be necessary to assess the validity of this statement.

References

- 1 J. N. Bradley and P. D. Greene, *Trans. Faraday Soc.*, **62** (1966) 2069.
- 2 B. B. Owens and G. R. Argue, *Science*, **157** (1967) 308.
- 3 Y. F. Y. Yao and J. T. Kummer, *J. Inorg. Nucl. Chem.*, **29** (1967) 2453.
- 4 L. Houch and D. N. Bennion, *J. Electrochem. Soc.*, **118** (1971) 1128.
- 5 N. Weber and J. T. Kummer, *Intersoc. Energy Convers. Engng. Conf.*, (1967) 913.
- 6 W. M. Latimer, *Oxidation Potentials*, 2nd Edn, Prentice Hall, Englewood Cliffs, 1952.
- 7 R. Schöllhorn, R. Kuhlmann and J. O. Besenhard, *Mater. Res. Bull.*, **11** (1976) 83.
- 8 J. O. Besenhard and R. Schöllhorn, *J. Power Sources*, **1** (1976/77) 267.
- 9 D. A. Winn, J. M. Shemilt and B. C. H. Steele, *Mater. Res. Bull.*, **11** (1976) 559.
- 10 M. B. Armand in W. Van Gool (ed.), *Fast Ion Transport in Solids*, North Holland, Amsterdam, 1973, p. 665.
- 11 G. D. West, *personal communication*.
- 12 H. Tannenberger, M. A. Cadman and M. Voinov, *Bienn. Meet. I.S.E.*, Marcousis, May 1975.
- 13 N. Platzer, *Bull Soc. Chim. France*, **117** (1961).
- 14 T. Dickinson, A. F. Povey and P. M. A. Sherwood, *J. Solid State Chem.*, **13** (1975) 237.
- 15 J. L. Sudworth, M. D. Hames, M. A. Storey, M. F. Azim and A. R. Tilley, in D. H. Collins (ed.), *Power Sources*, **4**, Oriel Press, Newcastle upon Tyne, 1973, p. 1.
- 16 J. T. Kummer, *Prog. Solid State Chem.*, **7** (1972) 141.
- 17 R. D. Armstrong, T. Dickinson and J. Turner, *J. Electroanal. Chem.*, **44** (1973) 157.
- 18 R. D. Armstrong, T. Dickinson and J. Turner, *Electrochim. Acta*, **19** (1974) 187.
- 19 T. Dickinson, *personal communication*.
- 20 T. Dickinson, A. F. Povey and P. M. A. Sherwood, *J. C. S. Faraday Trans. I*, **72** (1976) 686.
- 21 L. B. Ebert, R. A. Huggins and J. I. Braunen, *Carbon*, **12** (1974) 199.
- 22 M. Voinov and H. Tannenberger, *Electrochim. Acta*, **19** (1974) 959.