

Short Communication

Isopropoxide ion – a novel depolarizer for aluminium batteries

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Abstract

The effect of isopropoxide as a depolarizer in aluminium cells/batteries is reported. The open-circuit potential, short-circuit current and discharge behaviour of both Al–polypyrrole and Al–MnO₂ cells are improved significantly in the presence of isopropoxide. Isopropoxide ions are a better depolarizer than hydroxide ions. Galvanostatic polarization studies indicate that aluminium ions discharge at a higher potential in the presence of isopropoxide salt. The results indicate the possible use of isopropoxide ion as a depolarizer in practical aluminium batteries.

Introduction

Aluminium batteries have attracted considerable attention [1] during recent years because of possible applications in telecommunications equipment, electric vehicles and other electronic devices. Both saline and alkaline systems with MnO₂, Ag₂O, H₂O₂ or air cathodes have been investigated [1]. Molten-salt aluminium batteries are also well known [2]. The performance of such batteries, along with their polarization characteristics, has been recently summarized by Tuck *et al.* [3].

The objective of the present investigation is to examine the suitability of isopropoxide ion (iPO⁻) as an anode depolarizer for aluminium batteries. This has involved investigations with saline, or slightly alkaline, batteries coupled with conducting polymer or MnO₂ cathodes. Fabrication of a conducting polypyrrole cathode using permanganate ion (MnO₄⁻) as the doped anion is also reported.

Experimental

Electrolytes and depolarizers

Sodium isopropoxide was prepared by refluxing isopropanol (BDH) with metallic sodium (Merck, FRG). This resulted in the generation of hydrogen and the formation of a white solid. The latter was washed with dry distilled ether, re-crystallized from absolute ethanol, and kept in a dry box. Saturated KClO₃ (BDH) solution was used

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as the electrolyte for saline aluminium batteries. Alternatively, a mixture of KClO_3 , NH_4Cl (BDH, AR) and NH_4OH (MERCK) was employed as the electrolyte. De-ionized, double-distilled water was used as solvent.

Anode

Specification pure aluminium rod (Johnson-Matthey, UK) was used as the anode. The rod was degreased with dry distilled acetone, etched with dilute HCl solution, and washed repeatedly with distilled water.

Cathode

A carbon rod of the type used in commercial dry batteries (Nippo-Japan) was coated with a polypyrrole (PPY) film following the procedure described previously [4], but in this case permanganate ion (MnO_4^-) replaced picrate ion as the dopant. The cathode was fabricated by electro-oxidation of pyrrole (MERCK, FRG) in aqueous 0.006 M KMnO_4 solution. The black polymer film so formed was found to adhere well to the carbon and to have good electrical conductivity.

MnO_2 was prepared electrolytically, using a graphite anode and a stainless-steel cathode, from a solution of MnSO_4 (pH=4) at a current density of 20 mA cm^{-2} . The MnO_2 so prepared was removed from the graphite substrate, mixed with conducting paste, and then uniformly pressed onto the carbon rod. The MnO_2 cathode was stored in a dry box.

Cell assembly

Cells were prepared by dipping the cathode and the anode (separated by millipore-paper separator) in either saturated electrolyte solution (to provide a 'blank') or electrolyte containing saturated depolarizer solution in the ratio 4:1. The following four types of electrochemical cells were assembled.

Cell I Al| KClO_3 solution|PPY⁺ MnO_4^- , C

Cell II Al| KClO_3 + iPO^- solution|PPY⁺ MnO_4^- , C

Cell III Al| KClO_3 + iPO^- solution| MnO_2 , C

Cell IV Al| KClO_3 + (NH_4Cl + NH_4OH), pH = 7|PPY⁺ MnO_4^- , C

Results and discussion

The open-circuit potential (OCP) and the short-circuit current (SCC) of cells I–IV were determined at 27 °C with a digital multimeter; the results are given in Table 1. (Note, all potentials are reported with respect to a SCE.) It can be seen that the addition of iPO^- as a depolarizer causes a significant increase in the OCP of the cells. The effect is strongest in cell II, i.e., with PPY cathode. Only a slight increase in OCP of the cells. The effect is strongest in cell II, i.e., with PPY cathode. Only a slight increase is observed when OH^- is used as the depolarizer, i.e., cell IV. Thus, the iPO^- ion appears to be a better depolarizing agent for aluminium ions.

The SCC values are also significantly improved in the presence of a depolarizer. The maximum effect is observed with cell III i.e., the cell using MnO_2 as a cathode.

All cells were discharged at 1 mA for 60 min; the resulting behaviour is shown in Fig. 1. The values of the initial voltage drop are recorded in Table 1. A comparison of the drop in cell voltage under a 1 mA drawn for various aluminium cells [1] when

TABLE 1

Electrochemical parameters of aluminium cells at 27 °C

| Cell | <i>OCF</i> (V) | <i>SCC</i> (mA) | Initial voltage drop under drain of 1 mA (V) | Voltage (V) after 60 min of drain at 1 mA |
|------|-------------------|--------------------|--|---|
| I | 0.88 | 10.5 | 0.371 | 0.230 |
| II | 1.69 | 40.0 | 1.406 | 1.210 |
| III | 1.57 | 61.3 | 1.434 | 1.230 |
| IV | 0.97 | 22.4 | 0.633 | 0.530 |

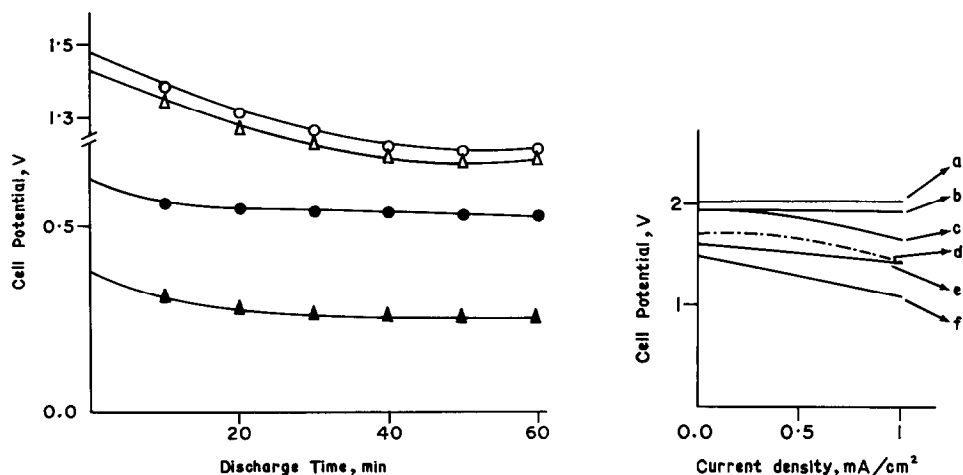
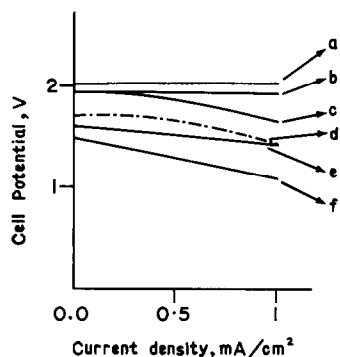


Fig. 1. Discharge curves for aluminium cells under 1 mA drain: (▲) cell I; (△) cell II; (○) cell III; (●) cell IV.

Fig. 2. Comparative performance of different aluminium cells showing drop in voltage due to 1 mA drain: (a) Al|Ag₂O (alkaline); (b) Al|air (alkaline); (c) Al|MnO₂ (saline); (d) Al|PPY (present work); (e) Al|air (saline); (f) Al|H₂O₂ (saline).



iPO⁻ ion is used as the depolarizer is given in Fig. 2. As expected, the discharge curves of these cells show that the plateau regions are markedly improved in the presence of the depolarizer. It is interesting to note that although an OH⁻ ion depolarizer cannot improve the OCP, the discharge plateau is comparable to that for a cell with an iPO⁻ ion depolarizer. The data of Fig. 2 are self explanatory and show that whereas the Al|Ag₂O (alkaline) battery is excellent (it has minimum *IR* drop), the performance of the present battery with an iPO⁻ ion depolarizer is comparable to that of an Al|air (saline) or an Al|H₂O₂ (saline) battery in terms of *IR* drop during drain.

To examine rechargeability of the cell, galvanostatic anodic polarization studies were undertaken using a 0.1 M Al₂(SO₄)₃ solution (pH=3), as blank, and a 0.1 M Al₂(SO₄)₃ solution containing iPO⁻ solution at pH 8. The curves are given in Fig. 3. The data indicate clearly that the Al ion is stabilized by the iPO⁻ ion. The shoulder on the curve, which probably indicates the onset of hydrogen evolution, is significantly reduced in the iPO⁻ medium. This may be due to the slight alkalinity of the latter.

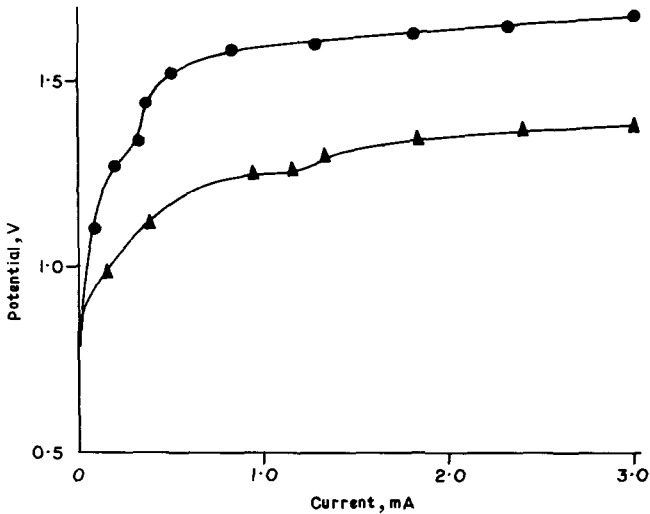


Fig. 3. Polarization curves for aluminium anode in combination with Pt cathode: (●) isopropoxide in 0.1 M $\text{Al}_2(\text{SO}_4)_3$; (▲) blank.

Conclusions

From the results of this preliminary investigation, it appears that isopropoxide salts improve both the OCP and discharge behaviour of aluminium cells/batteries. Galvanostatic polarization studies indicate that the discharge potential of Al^{3+} is increased significantly in the presence of iPO^- . The performance characteristics of polymer cathodes in these batteries are satisfactory and may be useful for the future development of light-weight, pollution-free batteries.

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