

Short Communication

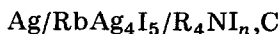
Comments on the Discharge Mechanism of Silver Iodide-Based Solid Electrolyte Cells

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In a recent paper in this journal [1], Lazzari, Rivolta and Bonino found, from their studies of the conductivity of mixtures of silver iodide and quaternary ammonium iodides, that no ionically conducting material was formed at room temperature. From this they deduced that in cells of the type



(where R_4NI_n is an alkyl ammonium polyiodide with $\text{R} = \text{CH}_3$ or C_2H_5 and $3 \leq n \leq 9$) the cathodic process must involve the formation of high ionically conducting material which is not derived from a primary discharge product of silver iodide.

We make the following observations:

(i) Lazzari *et al.* [1] follow Oxley and Owens [2] in stating that it is desirable for the cathodic discharge products to have a high ionic conductivity. This is not a mandatory requirement. The LiI cell, for example, has an electrode product with $\sigma = 10^{-7} \text{ S cm}^{-1}$. We have studied many cells involving silver or copper iodides with sulphonium or ammonium iodides as electrolytes. We find no increase in cell resistance over periods of several months when currents of up to $100 \mu\text{A cm}^{-2}$ are drawn continuously from cells of the type, *e.g.*, $\text{Ag}/7\text{AgI} \cdot (\text{CH}_3)_3\text{SI}/\text{I}_2$ -perylene.

In these cells, 4.5 g of electrolyte were used. Simple calculation shows that over a two month discharge period, if AgI were the primary reaction product, and were uniformly incorporated into the electrolyte, then the overall stoichiometry of the latter changes from an initial 84 mol% AgI, to 87 mol% AgI. This would decrease the conductivity from $2.7 \times 10^{-2} \text{ S cm}^{-1}$ to about $5 \times 10^{-2} \text{ S cm}^{-1}$ [3]. Even if AgI diffused into the first 10% of the electrolyte layer rather than being uniformly distributed, the conductivity would still be acceptable.

Although the electrolyte layer would increase in thickness and decrease in conductivity from addition of AgI, the current density could still be maintained.

(ii) On the assumption that AgI could not be the ultimate reaction product, Lazzari *et al.* [1] proposed two hypotheses for the formation of highly conducting materials. The first involved the primary formation of AgI which subsequently reacted to give the highly conducting material, and the second involved its direct formation. To test these hypotheses they measured the conductivity of the products obtained from the solid state reaction between commercially available AgI and alkylammonium *monoiodides* at various temperatures. They concluded that, below 85 °C, the rate of formation of highly conducting material was negligible. This does not necessarily preclude the reaction taking place at normal temperatures within a cell system because, among other factors, the electrochemically-formed reactants are in a different (and probably more advantageous) state of subdivision and contact and, also, the presence of an internal electric field could influence the kinetics.

(iii) In all the examples given by Lazzari *et al.* [1], the cathode materials are quaternary ammonium polyiodides, which could plausibly act as the source of quaternary ammonium iodide in the highly conducting product. Many examples exist, however, of successful AgI based cell systems using perylene-I₂ and other non-polyiodide cathodes, which cannot act in the same manner. The voltage of such cells has been generally found [*e.g.*, 4 - 7] to remain on a plateau for long discharge periods, indicating no severe rise in resistance of the cell.

In the absence of X-ray and other evidence, it seems difficult to join Lazzari *et al.* [1] in their firm conclusion that "the cathodic process does not involve the primary formation of silver iodide".

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References

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