

## Short Communication

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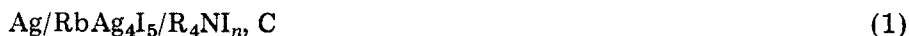
### On the Discharge Mechanism of Silver/Alkylammonium Polyiodide Solid State Cells

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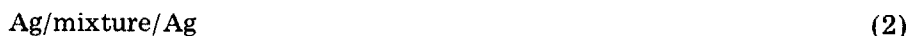
The cathodic discharge process for solid state cells of the type:



where  $\text{R}_4\text{NI}_n$  is an alkylammonium polyiodide with  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$  and  $n = 3 - 9$ , should involve, according to Oxley and Owens [1], the formation of materials having high ionic conductivity, such as  $\text{R}_4\text{NI} \cdot x\text{AgI}$ , with  $x = 5 - 7$ . A similar mechanism has been recently proposed for cells in which sulphonium polyiodides are used in connection with silver solid electrolytes based on sulphonium iodides [2]. In both cases the proposed mechanism is founded on the relevant experimental observation that the cell resistance is nearly constant during the discharge, while it should increase if silver iodide is formed at the cathodic interphase.

Two hypotheses can be considered: (i) silver iodide, formed as primary discharge product, does react with the alkylammonium iodide to form a high conductivity material; (ii) a high conductivity material is primarily formed.

Within a systematic study of the kinetics of the solid-state reactions between silver iodide and tetraalkylammonium iodides by conductivity measurements and microscope observations, with the reactants in the form of mixtures of powders and of separate pellets, respectively, we demonstrated that the rate of formation of high conductivity compounds is negligibly small at room temperature, even under the most favourable conditions (*i.e.* intimate mixture of the reactants). However, at higher temperatures the kinetics appear to be different as indicated in Figs. 1 and 2 which show the conductance as a function of time at different temperatures of symmetrical cells of the type:



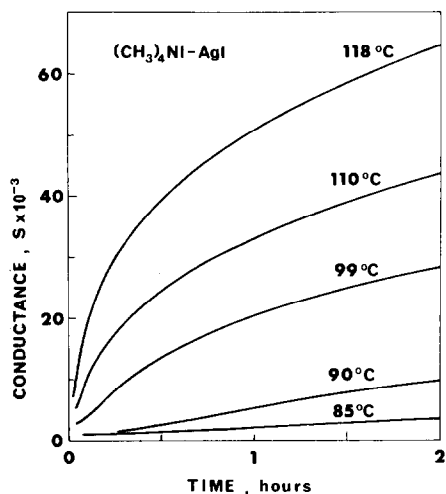


Fig. 1. Conductance vs. time of a mixture (CH<sub>3</sub>)<sub>4</sub>NI-AgI (mole ratio 0.13/0.87) at various temperatures.

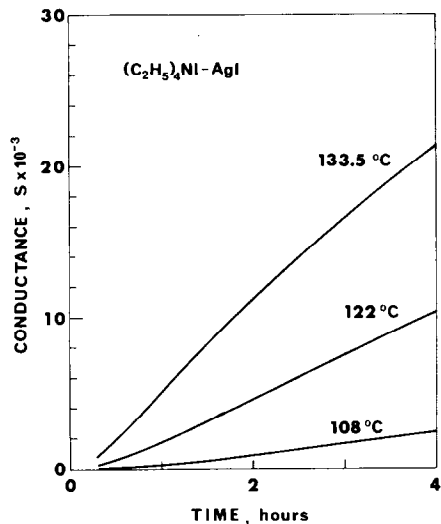


Fig. 2. Conductance vs. time of a mixture (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NI-AgI (mole ratio 0.13/0.87) at various temperatures.

The mixtures of AgI and the alkylammonium iodide had compositions corresponding to a mole fraction of AgI of 0.87\*. The mixtures have been prepared according to the method of Owens [4]. The pellets (0.7 g of mixture, 1.2 cm in diameter) obtained by pressing the powder at 2200 kg/cm<sup>2</sup> were kept at the chosen temperature in an inert gas atmosphere. The conductance was measured at 1592 Hz by a Wayne & Kerr B-331 MK11 bridge.

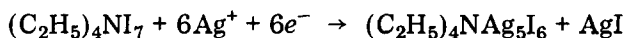
The plots show that it is necessary to reach a temperature > 85 °C to have a detectable rate of formation of the high conductivity products. At room temperature the rate of both reactions is negligible. It is therefore possible to conclude that in cells of type (1) the cathodic process does not involve the primary formation of silver iodide.

The results recently obtained by Kopchekchi *et al.* [5] seem to confirm the general validity of a mechanism implying the direct formation, through an electrochemical process, of materials having high ionic conductivity. These authors could indeed demonstrate, by potentiodynamic measurements, that in the case of the cell:



\*This composition corresponds, according to Geller and Lind [3], to the conductive phase (CH<sub>3</sub>)<sub>4</sub>N<sub>2</sub>Ag<sub>13</sub>I<sub>15</sub>. In the case of the system based on tetraethylammonium iodide, the composition of the conductive phase is not known from X-ray studies. The chosen value of  $x_{\text{AgI}} = 0.87$  is very close to the maximum in the conductivity-composition plot determined by Owens [4].

the cathodic discharge products are AgI and the solid electrolyte  $(C_2H_5)_4NI \cdot 5AgI$ . Apart from a possibly slightly different formulation of the conductive phase, the cathodic reaction:



may be considered. This appears to be in agreement with the discharge characteristics of a cell in which high conductivity complexes are formed by direct electrosynthesis. The hypothesis of the electrochemical generation of high conductivity species in a cell of this type put forward by Owens is therefore both experimentally confirmed and supported by other studies carried out since the original study.

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- 2 R. G. Linford, J. M. Pollock and C. F. Randell, in D. H. Collins (ed.), *Power Sources 6*, Academic Press, New York, 1977, p. 511.
- 3 S. Geller and M. D. Lind, *J. Chem. Phys.*, 52 (1970) 5854.
- 4 B. B. Owens, *J. Electrochem. Soc.*, 117 (1970) 1536.
- 5 L. G. Kopchekchi, A. M. Mikhailova and E. A. Ukshe, *Elektrokhimiya*, 12 (1976) 970.