

Improvement of solid electrolyte conductivity and cathodic properties of the $\text{Li}|\text{LiI}\cdot\text{H}_2\text{O}(\text{SiO}_2)|\text{PbI}_2$ electrochemical cell

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Abstract

The present investigation was carried out within the framework of the development of the $\text{Li}|\text{LiI}\cdot\text{H}_2\text{O}(\text{SiO}_2)|\text{PbI}_2$ rechargeable electrochemical cell of 2.8 V open-circuit voltage. The influence of various types of silica on the conductivity of the $\text{LiI}\cdot\text{H}_2\text{O}(\text{SiO}_2)$ solid electrolyte has been investigated. A comparison between different silica powders has been made and large differences in the investigated cell performance were observed. In the course of the above research it was noticed that the improved conductivity performance of silica is due to the presence of $-\text{OH}$ groups, i.e. silanol ($\text{Si}-\text{OH}$), on the surface. As a result of the above findings a considerable improvement of the preparation process of the investigated solid electrolyte was achieved and the conductance of $0.6\text{SiO}_2\cdot 0.4(\text{LiI}\cdot\text{H}_2\text{O})$ in the present study was $2.02\times 10^{-2} (\Omega \text{ cm})^{-1}$ at 25 °C.

Introduction

Liang was the first to reveal [1] the possibility of ionic conductivity improvement of LiI (by two orders of magnitude) by addition of Al_2O_3 . Owens and Hanson [2] investigated electrolytes based on $\text{LiI}\cdot\text{H}_2\text{O}$ with addition of large quantities of Al_2O_3 or SiO_2 . Hydrates of lithium halides which included Al_2O_3 or SiO_2 exhibited a large increase of conductivity in comparison with pure LiX . The conductivity dependence for $\text{LiX}\cdot\text{H}_2\text{O}\cdot\text{Al}_2\text{O}_3$ (or $\text{LiX}\cdot\text{H}_2\text{O}\cdot\text{SiO}_2$) has been investigated with variable water contents and showed the optimal conductance for a composition corresponding to lithium halide monohydrate (including LiF which is not known in the hydrate form).

$\text{LiI}\cdot\text{H}_2\text{O}$ has a conductivity [3] of $10^{-5} (\Omega \text{ cm})^{-1}$ which is two orders of magnitude higher than that of LiI and is dominantly ionic [4].

On addition of SiO_2 to $\text{LiI}\cdot\text{H}_2\text{O}$, a considerable improvement in the conductivity was achieved [5]. The conductance for $0.6\text{SiO}_2\cdot 0.4(\text{LiI}\cdot\text{H}_2\text{O})$ in the present study was $2.02\times 10^{-2} (\Omega \text{ cm})^{-1}$ at 25 °C.

The role of water in the conductivity process remains unclear. Additional findings of Liang *et al.* [6] showed that the conductivity of LiI could be improved by a factor of 500 by addition of Al_2O_3 . The conductivity enhancement mechanism in LiI water suspension containing SiO_2 or Al_2O_3 also remains obscure.

Likewise, many proposed models [3, 7–15] gave no plausible explanation of $\text{LiI}\cdot\text{H}_2\text{O}$ conductivity improvement on addition of SiO_2 .

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The present investigation was carried out within the framework of the development of the $\text{Li}|0.6\text{SiO}_2 \cdot 0.4(\text{LiI} \cdot \text{H}_2\text{O})|\text{phenothiazine}-\text{I}_2$ rechargeable electrochemical cell. In the course of the above research it was noticed that the improvement in the solid electrolyte conductivity was due to the $-\text{OH}$ groups on the SiO_2 surface.

A similar assumption was made by Maier [16] and very recently by Asai *et al.* [17] regarding Al_2O_3 .

Experimental

Materials and preparation

The $\text{LiI} \cdot \text{H}_2\text{O}(\text{SiO}_2)$ solid electrolyte was prepared by mixing the ingredients ($\text{LiI} \cdot \text{H}_2\text{O}$ (BDH, 98%); SiO_2 (different details in the text)) at different weight ratios. The weighing and the mixing were performed in a dry box at relative humidity less than 1%. SiO_2 was dried at 150 °C for 5 h before use. The cathode powder was prepared by mixing I_2 (Frutarom, analytical), phenothiazine (Abic, medical), RbAg_3I_4 and graphite (JMC) (or PbI_2 (BDH) instead of the phenothiazine-iodine mixture) at optimal quantities [18]. The preparation of the Li powder included dissolving its petrolate suspension (Lithium Corporation of America, 30% Li, 20 μm > 90%) in toluene (Frutarom, CP), and vacuum filtering while washing with ether (Bio-Lab, Absolute AR).

The IR spectra of pressed silica pellets mixed KBr (3.5 mg SiO_2 within 250 mg KBr) were recorded.

Cell construction and electrical measurements

The cell was constructed in the following way. The cathode layer was prepressed at a pressure of 320 kg/cm^2 in a 1.8 cm diameter anodized aluminium die, which contained a PVC ring 0.2 mm thick. The electrolyte layer was pressed until a maximum conductivity was measured at 1 kHz frequency using an Autoranging Conductometer. The electrolyte layer thickness was determined by means of a depth caliber. Finally, the 1.6 cm diameter lithium anode was pressed at a pressure of 720 kg/cm^2 . The electrical leads were spot-welded to tantalum disks which were pressed to the electrodes. The cell voltage was monitored using a Keithley 610B electrometer.

The cell construction and all electrical measurements were performed in a dry box at ambient temperature. The electrical leads of the cell were connected to various measuring instruments outside the dry box through proper feedthroughs.

Background, results and discussion

A $\text{Li}|\text{LiI} \cdot \text{H}_2\text{O}|\text{phenothiazine}-\text{I}_2$ electrical cell developed in our laboratory exhibited open-circuit voltage of 2.78–2.79 V and short-circuit current of about 0.2 mA/cm^2 at room temperature. Attempts to improve $\text{LiI} \cdot \text{H}_2\text{O}$ conductivity by addition of SiO_2 in the form of silica gel (Woelm Pharma, grain sizes 100–200 μm) resulted in electrochemical cells which exhibited short-circuit currents up to 10 mA/cm^2 (at room temperature) and an open-circuit voltage of 2.82–2.83 V. The relative quantities of electrolyte ingredients have been investigated. The optimal composition was $0.6\text{SiO}_2 \cdot 0.4(\text{LiI} \cdot \text{H}_2\text{O})$. The above electrolyte was prepared by mixing the ingredients ($\text{LiI} \cdot \text{H}_2\text{O}$ and SiO_2) at different weight ratios; the weighing and mixing were performed in a dry box at relative humidity less than 1%. Addition of silica gel to $\text{LiI} \cdot \text{H}_2\text{O}$ improved the conductivity

(by order of magnitude) but caused lowering of compactness. To avoid this difficulty silica powders of much smaller grain sizes (Aerosil-380, $0.007 \mu\text{m}$) were tried. This resulted in improvement of the compactness and chargeability properties but also caused considerable performance deterioration: short-circuit currents were reduced to about 1 mA/cm^2 , equivalent to conductivity decrease by an order of magnitude. These findings (including cell performance in discharge under variable loads) indicated that the various silica powders have different properties. Silica gel showed a clear advantage over Aerosil-380, but the effect of the large difference in grain sizes was not permit conclusive. According to the existing theories [7] smaller grains improve the cell performance up to a certain limit beyond which the effectiveness of the smaller grain size is reduced. In view of the above considerations, it was necessary to investigate properties of intermediate grain sizes within the range 0.007 to $100 \mu\text{m}$. Two additional kinds of silica were employed: fused silica and α -quartz (Sibelco)—both of grain sizes of $6 \mu\text{m}$. The electrolyte conductivity in both cases was lowered by about three orders of magnitude in comparison with silica gel to $6 \times 10^{-7} (\Omega \text{ cm})^{-1}$. It became clear, that pure silica did not contribute to the conductivity of $\text{LiI} \cdot \text{H}_2\text{O}$ but, on the contrary, lowered its value by about 2.5 orders of magnitude. Likewise, it became clear that an additional factor exists which influences the conductivity.

In view of the findings described above, it has been assumed that the improved conductivity performance of silica is due to the presence of $-\text{OH}$ groups, i.e. silanol ($\text{Si}-\text{OH}$), on the surface. IR spectral results combined with conductivity measurements (of pressed silica pellets mixed with KBr) clearly indicated that this assumption was correct (see Fig. 1). The evaluation of the properties of silica gel (or Aerosil-380), Sibelco and fused silica shows a full correlation between cell performance and concentration of $-\text{OH}$ groups, but the comparison between silica gel and Aerosil-380 shows a certain discrepancy. The smaller grain size in Aerosil-380 may be the cause of poorer performance. An additional finding in support of the influence of $-\text{OH}$ groups on the conductivity was given by using Kieselgel-60 ($63-200 \mu\text{m}$) treated at 960°C for 3 h [19]. As a result of the above treatment, $-\text{OH}$ groups disappeared, as was determined by IR. Silica treated in this way lowered the $0.6\text{SiO}_2 \cdot 0.4(\text{LiI} \cdot \text{H}_2\text{O})$ electrolyte conductivity from 4.5×10^{-4} to $1.4 \times 10^{-7} (\Omega \text{ cm})^{-1}$, however the compactness was very much improved.

The conductance improvement is most probably due to the acidic properties of silanol groups which give rise to the presence of H^+ ions on the silica surface.

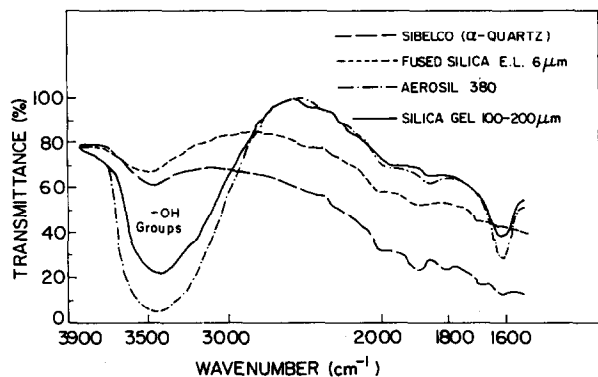


Fig. 1. IR spectra for different silica powders (conc. 1.4% in KBr).

In view of the above results a series of experiments was done to investigate the influence of water intake by silica on the electrolyte conductivity. Silica powder was kept, overnight in deionized water, followed by drying at 150 °C for 24 h. The increase of the concentration of $-OH$ groups on the silica surface improved the $0.6SiO_2 \cdot 0.4(LiI \cdot H_2O)$ electrolyte conductivity upto $2.02 \times 10^{-2} (\Omega \text{ cm})^{-1}$ (at 25 °C) for Aerosil-380.

A poor conductive electrolyte gave improved results in comparison even with the silica gel containing one handled under the same conditions. This was, probably, due to the large specific area of Aerosil-380 which permitted an absorption of large water quantities. The use of smaller particles also improved the performance and especially the rechargeability properties of the cell. The electrolyte layer was pressed (between silver electrolyte-containing electrodes) until a maximum possible conductivity was measured at 1 kHz frequency using an Autoranging conductometer.

The above-mentioned process gave no rise to electronic conductivity: open-circuit voltage of the investigated cell was even increased to 2.9 V this being the best evidence for the unwetted solid electrolyte. Experiments with 'wet' solid electrolytes performed in the framework of this investigation showed a considerable self-discharge accompanied by a decrease of the open-circuit voltage. This was due to a reaction between the Li anode and water inside the solid electrolyte. Formation of LiOH in the above process results in a deterioration of the electrical contact on the Li-electrolyte interface.

The investigated cell showed a good performance in discharge under variable loads of 0 to 100 k Ω and at constant currents of 0.25 to 1.5 mA/cm² (at room temperature) as compared with existing cells. However, the shelf-life of the above cells was only a few months. This was caused by iodine vapour diffusion through the electrolyte layer, leading to an undesirable reaction with Li to LiI in the anodic compartment of the cell. As a result, the capacity of the cell decreased and internal resistance increased.

The shelf-life of the cell was improved by using PbI₂ as an active cathode material. According to existing literature [20, 21] PbI₂ is an active cathodic material which may improve the shelf-life, but will cause a considerable decrease of open-circuit voltage from 2.8 to 1.9 V.

A $Li|0.6SiO_2 \cdot 0.4(LiI \cdot H_2O)|PbI_2$ electrochemical cell of 2.8 V open-circuit voltage and cathodic properties close to those of phenothiazine-iodine, which exhibits excellent cathode performance, was obtained by charging from an external power source. The above-mentioned charging process turns PbI₂ to an amorphous compound (as determined by X-ray diffraction) which retains excellent storage properties.

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