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Molten salt secondary battery using molten iodides

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Molten salt secondary batteries are a very interesting way to power electric vehicles. One of their advantages is the high conductivity of molten salts. The more interesting system seems to be Li-alloy/ FeS₂. Furthermore, the ability of building bipolar cells enables very high specific capacity and power outputs to be obtained. The main disadvantage of such batteries is the high temperature of operation, generally about 400°C. Our purpose is so to study molten salts which have a lower melting point than this. The eutectic LiI–KI, which melts at 280°C, has been chosen for study. Firstly, we have shown that this eutectic is thermally and electrochemically compatible with the classical LiAl/FeS₂ system. Moreover, the electrical conductivity of this electrolyte is quite comparable with that of the standard LiCl–KCI eutectic.

The experiments we have run have shown what appears to be a self-discharge phenomenon. However, the high rate of this reaction has indicated that this is not just self-discharge. Further investigations have shown that the use of other cathodes, known to be more stable, have given no such effects changes. The use of aluminium, as anodic material, has shown clearly that this metal is corroded by molten iodides.

We next demonstrated that the lithium–aluminium alloy is also corroded by molten iodide. This difficulty has been overcame by replacing lithium–aluminium by a lithium– silicon alloy.

Finally we have shown that the system $LiSi/LiI-KI/FeS_2$ is as good as $LiAI/LiCI-KCI/FeS_2$, even though it operates at a lower temperature. Our next step is to use the eutectic LiI-KI-CsI, which has a melting point lower than 230°C.

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P4

Thermoelectric properties of electrochemical systems

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A detailed analysis has been carried out on the thermoelectric properties of electrochemical systems comprising:

- 1. redox components, for example $Pt/Fe^{2+}/Fe^{3+}/Pt$
- 2. acid solutions with hydrogen electrodes
- 3. copper, nickel, zinc, and cadmium salt solutions with corresponding metal electrodes.

The influence of the temperature difference, the nature of the electrolyte solution and its concentration upon the electromotive force (EMF) of non-isothermal systems, Seebeck coefficient, thermoelectric potential and parameters of transfer processes in a liquid phase have been examined. It was shown that increasing the number of methyl groups in dibasic organic acids led to a decrease in the thermal flow contribution to the ion flow in non-isothermal systems with redox components, The increase in EMF for thermoelectric power sources with infinitely diluted aqueous solutions of mineral acids, or with redox components, is connected to the decrease of the acid's anion heat transfer.

A mathematical model describing the EMF dependence on a liquid phase concentration, electroconductivity, proton transference number and diffusion coefficient has been elucidated for non-isothermal systems based on hydrochloric, sulfuric, and orthophosphoric acid. A correlation between the evolution of EMF with the electrolyte concentration in the above systems and the diagrams of fusion, viscosity, and electroconductivity has been established and discussed. Maximal values of EMF for thermoelements with hydrogen electrodes correlate well with the maximal melting temperature of the hydrate. Using the experimental data, values of both the homogeneous thermoelectric potential for some salt-water systems with metal electrodes, and entropies of electrochemical, diffusional and migrational transfer of protons in acid solutions have been calculated. It was demonstrated that the imposition of a regulated temperature difference between electrodes considerably improved the parameters of hydrogen-oxygen fuel cells.

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P5

Performance of 2,4 dinitrophenol as positive electrode in a magnesium reserve battery

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Magnesium is an interesting anode battery material with many advantages such as its high standard potential of -2.37 V, low cost, good low temperature performance due to exothermic corrosion reactions during discharge etc. On the other hand, organic aromatic nitro compounds, as they undergo multielectron transfers of up to 18 during discharge, give high energy densities (up to 2 Ah g^{-1}) in comparison with conventional inorganic battery depolarizers like MnO₂, HgO, CuO, AgO etc. Hence, it is worthwhile fabricating and studying the performance of a battery system combining magnesium and 2,4-dinitro phenol (DNP) using aqueous halide electrolytes like MgCl₂, MgBr₂ and Mg(ClO₄)₂. This poster describes the preparation of DNP cathodes after standardization of the cathode mixture. One volt, one Ah Mg/DNP cells were assembled using the above cathode in conjunction with AZ31 magnesium alloy anodes and discharged at current densities of 1.7, 3.3, 5.6 and 6.6 mA cm⁻² in 2 M MgCl₂, MgBr₂ and $Mg(ClO_4)_2$. Cyclic voltammagrams of DNP were recorded in 2 M Mg(ClO₄)₂ at various sweep rates and concentrations in order to understand the reduction behaviour. This study suggests that DNP is a capable organic compound for use as cathode material in magnesium reserve batteries.

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P6

Rechargeability of natural manganese dioxide (NMD) modified by Bi_2O_3

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It has been reported in the literature that modified MnO₂ cathode materials containing bismuth allow multiple rechargeability over a two-electron capacity. All the reported researches are related to chemically or physically modified materials starting from high purity MnO₂ This work reports some results obtained with a natural manganese dioxide (NMD) with starting composition of 45% Mn, 15% Fe, 0.6% Si and 1.7% Al, which was modified by the addition of Bi₂O₃. X-ray diffractions show that this material has different crystallographic phases, among which pyrolusite is predominant. The reduction reversibility of NMD and NMD/Bi in 9 M KOH has been studied by slow scan voltammetry and constant current discharge and recharge. The results have shown good rechargeability and a discharge reaching 80-95% of the theoretical two-electron capacity in each cycle for the natural manganese dioxide modified by Bi₂O₃.

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Investigation of the system: lithium accumulator and a battery of solar cells on a long-cycling regime

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The aim of this work was to study the combined influence of polarization characteristics of lithium accumulators and a battery of solar cells and the cycling characteristics of lithium accumulators when charged from batteries of solar cells (BSC).

Tests were carried out with lithium accumulators having operating voltages of 3.0 V (Li– MnO_2) and 4.0 V (Li– $LiMn_2O_4$). Manganese oxides, synthesized in our laboratory by different methods, were used as cathode materials. The lithium accumulators were made as both coin (2325) and spiral-wound (R 20 size) cells.

Changes in the internal resistance of the cells at different stages of cycling regime were calculated from impedance measurements taken in the frequency band: 0.2 Hz-200 kHz.

The investigations showed how the charging characteristics of the lithium accumulators depended on the conditions of BSC illumination, the characteristics of BSC, the electrochemical properties of the synthesized manganese oxides and the composition of the non-aqueous electrolyte.

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P8

Influence of the composition of non-aqueous polymer electrolytes on the characteristics of the electrode / electrolyte interface and the efficiency of their use in lithium accumulators

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The aim of this work is to study the influence of the chemical nature of polymers, lithium salts and aprotic solvents on the conductance of non-aqueous electrolytes, on the interaction with electrode materials, system stability