

$f(X,t,U)$  is the density of heat sources at point  $(x, y, z)$  at time  $t$ .

The model takes into account:

- heating by means of pyrotechnical mixture or electric heater;
- possible melting of substances making up a source;
- changes of initial materials in the course of operation of the source;
- transference of heat inside and outside the case of the source via all possible mechanisms in accordance with the heat balance equation;
- liberation of heat in the course of operation from ohmic and polarization resistances and in the form of Peltier heat.

The thermal battery comprises flat unitary elements between which heaters are arranged. The battery is housed in a sealed case provided with internal heat insulation. Thus, the battery includes materials having diversified thermo-physical characteristics. The model covers the study of cylindrical batteries for which the three-dimensional thermo-conduction problem is readily reduced to a two-dimensional one. For the calculation of heat escape from the battery surface into the environment, a system of Napier-Stokes equations was designed. These take into account convection and various rates of forced cooling by atmospheric air at various temperatures. The boundary conditions correspond to either the absence of any environment, or to the placement of the battery in a wind tunnel.

Using the balance method, a differential scheme (taking into account the discontinuity of the first kind of thermo-physical characteristics of the simulation field) was synthesised on a non-uniform grid in the axial plane of the battery. Conditions for convergence of this scheme were found and the convergence itself was proved. For the purpose of reducing the number of operations per node without loss of accuracy, the scheme was transported into a so-called economical one which is solved by sweeping through lines and columns.

In accordance with the mathematical model, a programme was compiled enabling one to calculate a current source of a filter-press type design employing a Li/NiCl<sub>2</sub> couple. Input data for this model are:

- temperature dependences of thermodynamic potentials, densities, thermal capacities, thermal conductivities and resistivities of materials;
- polarization characteristics of anodic and cathodic materials;
- external load resistance, temperature and rate of flow of atmospheric air (these can vary in the course of battery discharge);
- geometrical dimensions of battery in the axial plane.

Output data are: temperature fields, battery current and voltage.

The programme was used to calculate a current source based on the Li/NiCl<sub>2</sub> couple. Good agreement has been obtained with the prototype. The programme offered a reduction in the number of tests required in the course of devel-

opment of a thermal battery for a specific technical project from 10 to 15 down to 3 to 4.

## P28

### Electron transfer in the molten salt systems: CuCl–CuCl<sub>2</sub>–LiCl and CuCl–CuCl<sub>2</sub>–NaCl

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In view of the growing interest in high-temperature storage batteries, there arises an urgent demand for investigations of new chemical materials capable of satisfying the needs of modern technology.

One such promising material is the CuCl–CuCl<sub>2</sub> salt melt that can be used as cathodic material in high-temperature chemical current sources (HTCCS). Earlier we have established that such a system in the temperature range 800–1000 K and at a pressure  $P_{\text{Cl}_2} =$  one bar, possesses an electronic conductivity 2.5 to 3 times the ionic.

This property, together with good thermodynamic characteristics of the system, gives promise that the power characteristics of HTCCS can be increased considerably.

In the course of any current-producing reaction, for example, in lithium or sodium HTCCS:



In the cathodic half-cell there accumulates a component not participating in the electron transfer of lithium or sodium chloride. This changes the electrochemical and physiochemical properties of the melt.

The purpose of this investigation was the measurement of density, ratio of concentrations of mono- and divalent copper, electrical conductivity and electron transfer numbers of the CuCl–CuCl<sub>2</sub> ionic-electronic salt melt, diluted with lithium chloride or sodium chloride (0 to 90 mole%), over the range  $T = 750\text{--}1000$  K and at  $P_{\text{Cl}_2} =$  one bar. We have used an original technique of ours, based on the non-correspondence of current output to Faraday's law, to measure electron transfer numbers. Electrical conductivity was measured using the standard capillary method and a cell with a known constant.

The ratio of concentrations of monovalent and bivalent copper was determined by chemical analysis of specimens selected by the quick quenching method. Density was measured by the dilatometric method.

The electronic and ionic components of electrical conductivity were calculated using experimental data.

The results show that the introduction of the lithium or sodium chloride into the CuCl–CuCl<sub>2</sub> melt leads to a drop in electronic conductivity. The introduction of sodium chloride

produces a greater drop in the electronic component than does lithium chloride. Nevertheless, even with sufficiently large dilutions the electron transfer remains considerable.

This experimental fact shows great promise for the use of CuCl–CuCl<sub>2</sub> melt as a cathodic material in high-temperature batteries employing Li/CuCl–CuCl<sub>2</sub> and Na/CuCl–CuCl<sub>2</sub> electrochemical systems.

We used the Nernst-Einstein equation to calculate the effective values of electron diffusion coefficients. The latter greatly exceed the values of Li<sup>+</sup> and Na<sup>+</sup> diffusion coefficients, usual for chloride melts, with dilution they drop in value and gradually become equal to zero.

We examined various mechanisms of transfer of electrons from cation Cu<sup>+</sup> to Cu<sup>2+</sup> in the investigated systems. It was assumed that the contribution to the electron transfer is made not by the direct interaction between cations Cu<sup>+</sup> and Cu<sup>2+</sup> but by their interaction through the medium of a Cl<sup>–</sup> anion.

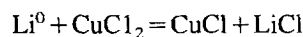
## P29

### High temperature lithium storage battery with an electron-conducting CuCl–CuCl<sub>2</sub> melt as cathodic material

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When a power source based on Li/CuCl<sub>2</sub> discharges, there takes place an accumulation of lithium chloride in the cathodic half-element in accordance with the current-producing reaction:



During recharging a reverse process occurs. In this investigation we studied cathodic and anodic polarization at the glassy carbon electrode in the CuCl–CuCl<sub>2</sub>–LiCl melt as a function of temperature and lithium chloride concentration at atmospheric pressure in chlorine. Measurements have shown that cathodic polarization in melts having considerable copper chloride concentrations is practically equal to zero over the current density range of 0 to 10 A cm<sup>–2</sup> while the anodic polarization is two orders of magnitude lower than that measured for purely ionic melts. Such values of polarization are explained by the presence of electronic conductivity together with ionic. We have also established that polarization measured relative to the reference electrode, filled with a purely ionic melt, has substantially higher values than the same polarization measured relative to the glassy carbon electrode immersed directly into the CuCl–CuCl<sub>2</sub>–LiCl melt. In this work we have shown that Wagner's notions of emf of electrochemical cells having ionic-electronic conductivity, developed by him for solid electrolytes, are applicable to melts studied by us. Wagner's equations were used to calculate

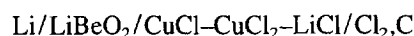
electron transference numbers. Within measurement error limits they coincided with measured values as regards non-correspondence of current output during electrolysis of these melts according to Faraday law. The most interesting experimental fact is that even with very high degrees of dilution of the CuCl–CuCl<sub>2</sub>–LiCl mixture with lithium chloride (up to 70 mol.%) the electron transference number has a significant value (0.25 to 0.30).

In comparison with the sodium-sulphur battery the one employing a Li/CuCl<sub>2</sub> system has the following advantages:

- about 1.2 V higher;
- no cathodic polarization;
- low electrolyte resistance in each half-cell because of electron transfer;
- possibility of reducing polarization at the Li/solid electrolyte and solid electrolyte/melt interfaces as a result of temperature increase.

A drawback of the Li/CuCl<sub>2</sub> system is that redox-potential E<sub>Cu<sup>2+</sup>/Cu<sup>+</sup></sub> drops sharply as the CuCl<sub>2</sub> changes into CuCl. However, taking into account the above-mentioned advantages, the specific power of a high-temperature battery using Li/CuCl<sub>2</sub> can be 4–5 times as great as that of the sodium-sulphur battery.

On the basis of results obtained, a laboratory model of the storage battery using two types of electrochemical cells was constructed:



Ten charge-discharge cycles were carried out. No deterioration of characteristics was noticed. The polarization of the cathodic half-element was zero. The test results give hope that a storage battery using CuCl–CuCl<sub>2</sub> melt will be developed with the following specific characteristics: energy density — 150 Wh kg<sup>–1</sup>; power density — 800 W kg<sup>–1</sup>.

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### Investigation aimed at development of a high-temperature lithium/air storage battery

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Power sources for battery-driven vehicles of the future must have high specific characteristics: specific energy not less than 200 Wh kg<sup>–1</sup>, peak specific power not less than 700 W kg<sup>–1</sup>.

Traditional storage batteries and those being developed for these purposes, except for sources having polymer electrolyte, will not be able to give a specific energy higher than 200 Wh kg<sup>–1</sup>. One of the main reasons is the low theoretical specific energy, as a rule less than one kWh kg<sup>–1</sup>, character-