

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.

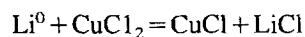
## P29

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

A.N. Yolshin, G.G. Arkhipov, V.V. Zakharov and N.N. Batalov

*Institute of High-Temperature Electrochemistry, Urals Branch of the Russian Academy of Sciences, Ekaterinburg, Russia*

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

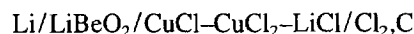
electron transference numbers. Within measurement error limits they coincided with measured values as regards non-correspondence of current output during electrolysis of these melts according to Faraday law. The most interesting experimental fact is that even with very high degrees of dilution of the 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>.

## P30

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

N.N. Batalov and G.G. Arkhipov

*Institute of High-Temperature Electrochemistry, Urals Branch of the Russian Academy of Sciences, Ekaterinburg, Russia*

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-

istic of the traditional oxidizer-reducer electrochemical couples. A promising system for high-energy storage batteries is one using lithium/oxygen (air). Its theoretical specific energy is about  $4.5 \text{ kWh kg}^{-1}$ . If we do not take into account the oxidiser mass, i.e. if we use atmospheric air, the theoretical specific energy amounts to  $10 \text{ kWh/kg}$ .

A still higher specific energy can be obtained in the boron/oxygen and beryllium/oxygen systems only. However, economic, ecological and electrochemical considerations prohibit the use of such systems in practice. Three options of storage batteries using the lithium/oxygen (air) system are possible:

1. lithium/solid lithium-conducting electrolyte/molten electrolyte/oxygen electrode.
2. lithium (alloy)/molten electrolyte/solid oxygen-conducting electrolyte/oxygen electrode.
3. lithium/polymer lithium-conducting electrolyte/aqueous solution of lithium hydroxide/oxygen electrode.

The right-hand half cells are analogues of oxygen half-cells in fuel cells having carbonate, solid-oxide and alkali electrolytes. The left-hand half-cells are analogues of lithium half cells of the sodium/sulphur, lithium-iron disulfide and lithium-polymer batteries.

Option 2 has been studied. Its drawback is the thermodynamic incompatibility of the solid and molten electrolytes since the reaction product  $\text{Li}_2\text{O}$  dissolves in the melt and interacts with the acid oxides of the solid electrolyte.

Option 1 is free of this drawback since it is possible to choose a solid electrolyte which is, at the same time, stable in respect of molten lithium and the oxygen-containing melt.

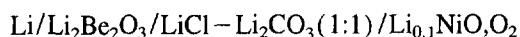
Thermodynamic calculations show that double oxides of lithium and beryllium, aluminium, yttrium, as well as of some lanthanides, show promise as possible lithium-conducting electrolytes stable in respect of lithium, in as much as the criterion of stability is fulfilled:

$$\Delta_f G_T^0(\text{Li}_2\text{O}) > \Delta_f G_T^0(\text{Me}_x\text{O}_y)$$

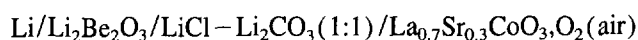
where  $\Delta_f G_T^0$  is the Gibbs energy of formation of lithium oxide and the oxide of the above mentioned metals.

Employing lithium beryllates and aluminates, we have synthesized a number of electrolytes with  $\text{Li}^+$  conductivity of  $3\text{--}10 \times 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $500\text{--}600^\circ\text{C}$  which do not interact with melts containing lithium oxide. Melts have been found in which about 10 mol.% of lithium oxide dissolved.

On the basis of these investigations, laboratory models of batteries have been developed in accordance with the following schemes:



and



The working temperature is  $580\text{--}600^\circ\text{C}$ . The construction of the investigated batteries is similar to that of the sodium-sulphur battery. Nickel oxide and ion ( $\text{O}^{2-}$ )-electron conductor — lanthanum and strontium cobaltite — materials traditionally used in carbonate fuel elements — have been chosen as materials for the oxygen electrode. This permits one to give up the gas-diffusion type of electrode, inasmuch as the oxygen is carried to the electrode/molten electrolyte interface via a solid specimen (phase) of the  $\text{O}^{2-}$  and  $2p^+$  kind.

Both types showed approximately the same discharge characteristics: voltage 2 V, current density of  $100 \text{ mA cm}^{-2}$  as referred to the area of the solid electrolyte separator.

The charging was carried out potentiostatically at a voltage of 3. The number of discharge-charge cycles attained was ten. The solid electrolyte separator was not affected by corrosion or damage.

The comparison between these options and sodium/nickel dichloride and sodium/sulphur permits one to believe that in practice their specific capacity should be higher than  $200 \text{ Wh kg}^{-1}$ .