

precise termination method and safety protection in addition to that provided during battery manufacture.

Pulse current, with duty cycle of 5 to 1, is used until maximum voltage is reached. The pulse amplitude is dropped at this point until maximum voltage is reached one more time. This process is repeated until the value of a predetermined minimum current is reached. This procedure excludes staying too long with constant voltage and thereby decreasing the probability of electrolyte decomposition, without substantially sacrificing charging capacity and charging time. The rest period in the TBM charging profile is used for measuring open-circuit voltage (OCV), also ohmic and chemical polarization. Control of these parameters allows us to recognise hard, soft and chemical shunts as well and to make some adjustments to the charging profile.

The potential chemical shunt for example, which is specified as the reaction between electrolyte and metallic lithium, can be recognized from measurement of chemical polarization, which is inversely dependent on cell temperature. The battery response to an internal source of heat, from chemical polarization, is much faster than that of an external thermistor. Hard shunt identification is provided monitoring for a fast drop in the charging voltage, with the identification of soft shorts by monitoring the change in OCV. The conditions for creation of dendrites are monitored as a rise in chemical (concentration) polarization and the charging current is then tapered as necessary.

The cell equalization procedure includes measuring the OCV of individual cells, both at the beginning and end of charge, to identify any cell imbalance.

The rate of response during charging for a soft short is about one second, including conformation time, and less than 20 ms for a hard shunt. The measurement accuracy is ± 8 to 10 mV for full battery voltage.

The charge process provides a highly efficient transfer of energy from any power supply (linear or switching) to the battery terminals by the use of pulse width modulation.

The lithium charging algorithm can be used with regular microcontroller parameters: 8-bit word length, a frequency of at least 2 Mhz, four or more ADC inputs and at least one 8-bit parallel port.

P26

The morphology of microporous polyethylene separators and its significance for the performance of lithium batteries

G.H.M. Calis, A.P.M. Daemen, N.S.J.A. Gerrits,
J.T. Smedinga

DSM Solutech BV, Eisterweg 4, 6411 PN Heerlen, The Netherlands

Solupor™ is a novel microporous (ultra) high molecular weight polyethylene membrane, fabricated in standard grades

with base weights ranging from 7 to 16 g m⁻² and mean pore sizes ranging from 0.1 to 2.0 μm and a porosity of 80 to 90%. The suitability of Solupor™ membranes as separator material in lithium batteries is demonstrated. These membranes have good wettability and thermal stability and pass voltage breakdown testing.

McMullin numbers are reported, ranging from 4 to 20 and tortuosities ranging from 1.8 to 4.1.

Electrical resistance is lowest for membranes with the highest pore size. Solupor™ membranes were tested in primary Li/MnO₂ cells and have load characteristics equal to or slightly better than commercial reference materials.

A special Solupor™ grade has been developed for an application in a battery production process for R6-size ("AA") cells, in which the separator experiences high winding forces. At present, another special grade is under development, being a membrane with thermal shutdown capability and high permeability.

P27

Model of a powerful high-temperature primary battery

D.N. Nikitin, A.N. Yolshin, V.V. Zakharov, N.N. Batalov,
I.V. Khmelevsky

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

The design of thermal chemical current sources (TCCS) for the solving of specific technological problems necessitates testing a large number of arrangements having various characteristics. One of the ways of reducing the volume of preliminary experimental work is computer simulation.

A mathematical model of thermal regimes of thermal batteries of filter-press design with cylindrical symmetry has been developed. This model is described by a heat balance equation in a region G with boundary S:

$$\begin{aligned} & \iiint_G c(X,U) \cdot \rho(X,U) \{U(X,t_2) - U(X,t_1)\} dV \\ & = \int_{\tau,S} \phi\{W(X,t,U) \cdot d\sigma\} + \iiint_G \int_{\tau} f(X,t,U) dt dV \\ & W_{\alpha}(X,t,U) = -\lambda(X,U) \cdot \frac{\partial U(X,t)}{\partial x_{\alpha}} \end{aligned}$$

where:

$c(X,U)$ is the thermal capacity at point (x, y, z) , having temperature U ;

$\rho(X,U)$ is the density at point (x, y, z) ;

$U(X,t)$ is the temperature at point (x, y, z) , at time t ;

$W_{\alpha}(X,t,U)$ is the heat flow in the direction of Ox_{α}

$\lambda(X,U)$ is the thermal conductivity at point (x, y, z) ;

$f(X,t,U)$ 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/NiCl₂ 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/NiCl₂ 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–CuCl₂–LiCl and CuCl–CuCl₂–NaCl

P. Yu. Shevelin, A.N. Yolshin, A.A. Red'kin,
N.G. Molchanova and N.N. Batalov

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

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–CuCl₂ 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 $P_{\text{Cl}_2} = \text{one bar}$, 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–CuCl₂ ionic-electronic salt melt, diluted with lithium chloride or sodium chloride (0 to 90 mole%), over the range $T = 750\text{--}1000\text{ K}$ and at $P_{\text{Cl}_2} = \text{one bar}$. 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–CuCl₂ melt leads to a drop in electronic conductivity. The introduction of sodium chloride