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Technical Report on Galvanic Cells With Fused-Salt Electrolytes

A technical report has been presented on sodium and lithium cells using fused-salt electrolytes—the type which might be used in converting heat to electricity. The report includes a discussion of the thermally regenerative galvanic cell and the secondary bimetallic cell for storage of electricity. This information may be of interest to electrochemists in the fuel cell and battery field, and to physicists, chemists, and engineers concerned with energy conversions.

Most of today's energy-conversion research effort is in the area of converting thermal energy to electrical energy. The thermally regenerative galvanic cell is important for energy conversion in applications requiring silence, simplicity and unattended operation. Such a system is compatible with high-temperature nuclear reactors and radioisotope heat sources.

The thermally regenerative bimetallic galvanic cell system consists of a galvanic cell to produce electricity, a regenerator to thermally decompose the product of the cell reaction into the original reactants, and a heat exchanger to conserve heat. The cells discussed in the report use a relatively volatile liquid-alkali metal having a low electronegativity for the anode and a relatively nonvolatile liquid metal of high electronegativity for the cathode. In the cell portion of the system, the anode metal is oxidized to form a cation which migrates through the fused-salt electrolyte to the cathode, where it is electrochemically reduced, forming an alloy with the cathode metal. The electrons released at the anode travel through the electrical circuit, finally arriving at the cathode to complete the circuit. The cathode alloy circulates from the cell to a high-temperature regenerator (1050° to 1600°K), where the anode metal is vaporized away from the cathode metal. The anode metal vapor passes to a relatively cool condensation zone, and the condensate

is returned to the anode compartment of the cell, completing the cycle.

This process is Carnot-cycle limited; the maximum theoretical efficiency of the overall conversion process is determined by the temperature of the regenerator and the condenser.

In selecting suitable anode metal-cathode metal pairs, the proper electronegativity differences must be selected so that the alloy can be separated at reasonable regenerator conditions while still maintaining an appropriate cell voltage (0.5 to 0.7V). Furthermore, the electrode materials and the electrolyte should melt at low temperatures to provide a low heat-rejection temperature and a high Carnot-cycle efficiency.

Significant differences exist in the properties of the cells and systems, depending upon the alkali metal used as the anode. Of the alkali metals, lithium and sodium exhibit the highest cell emf values and have the best physicochemical properties for use in galvanic cell systems. Na-Bi, Na-Pb, Li-Sn and Li-H₂ were found suitable for thermal regeneration.

The lithium-tin system is currently under investigation as a thermally regenerative bimetallic cell. Because of the very low vapor pressure of tin relative to that of lithium, an excellent separation of lithium from tin can probably be accomplished in a simple, single-stage regenerator with no reflux. Furthermore, the regenerator should operate above 1300°K, while the cell should operate near 600°K, providing an overall system efficiency near 30%. This is not possible with any presently known sodium system.

In addition to the conversion of thermal energy to electricity, means for the storage of electrical energy are also important. The secondary cell stores electrical

(continued overleaf)

energy by converting it to chemical energy, and then reconverting the chemical energy to electrical energy on demand. Bimetallic cells with fused-salt electrolytes can be operated as secondary cells, which can be charged and discharged at high rates.

For secondary cells with high energy-to-weight ratios, the systems investigated were those with lithium and sodium and sodium anodes because they are higher in the electromotive series than other alkali metals and have the lowest equivalent weights. Systems found suitable for use as secondary cells were Li-Te, Li-Se, Na-Bi, Li-Bi, Li-Sn, Li-Cd, Li-Zn and Li-Pb.

The lithium systems have been favored for secondary cells because of the higher cell voltages, lower operating temperatures (615° to 725°K for lithium cells versus 810° to 900°K for sodium cells), and generally lower solubilities of lithium and lithium intermetallic compounds in the electrolyte.

Notes:

1. Further information is available in "Galvanic Cells With Fused-Salt Electrolytes," ANL-7316, Argonne National Laboratory, November 1967. This report is available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151; price \$3.00 each (microfiche copies, \$0.65 each).

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