



## NiF<sub>2</sub>/NaF:CaF<sub>2</sub>/Ca Solid-State High-Temperature Battery Cells

Solid-state design mitigates parasitic self-discharge reactions to facilitate longer operational life.

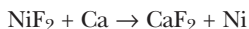
NASA's Jet Propulsion Laboratory, Pasadena, California

Experiments and theoretical study have demonstrated the promise of all-solid-state, high-temperature electrochemical battery cells based on NiF<sub>2</sub> as the active cathode material, CaF<sub>2</sub> doped with NaF as the electrolyte material, and Ca as the active anode material. These and other all-solid-state cells have been investigated in a continuing effort to develop batteries for instruments that must operate in environments much hotter than can be withstood by ordinary commercially available batteries. Batteries of this type are needed for exploration of Venus (where the mean surface temperature is about 450 °C), and could be used on Earth for such applications as measuring physical and chemical conditions in geothermal wells and oil wells.

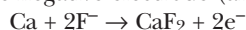
All-solid-state high-temperature power cells are sought as alternatives to other high-temperature power cells based, variously, on molten anodes and cathodes or molten eutectic salt electrolytes. Among the all-solid-state predecessors of the present NiF<sub>2</sub>/NaF:CaF<sub>2</sub>/Ca cells are those described in "Solid-State High-Temperature Power Cells" (NPO-44396), *NASA Tech Briefs*, Vol. 32, No. 5 (May 2008), page 40. In those cells, the active cathode material is FeS<sub>2</sub>, the electrolyte material is a crystalline solid solution of equimolar amounts of Li<sub>3</sub>PO<sub>4</sub> and LiSiO<sub>4</sub>, and the active anode material is Li contained within an alloy that remains solid in the intended high operational temperature range.

The chemical reactions during discharge of an NiF<sub>2</sub>/NaF:CaF<sub>2</sub>/Ca cell are the following:

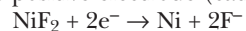
Overall:



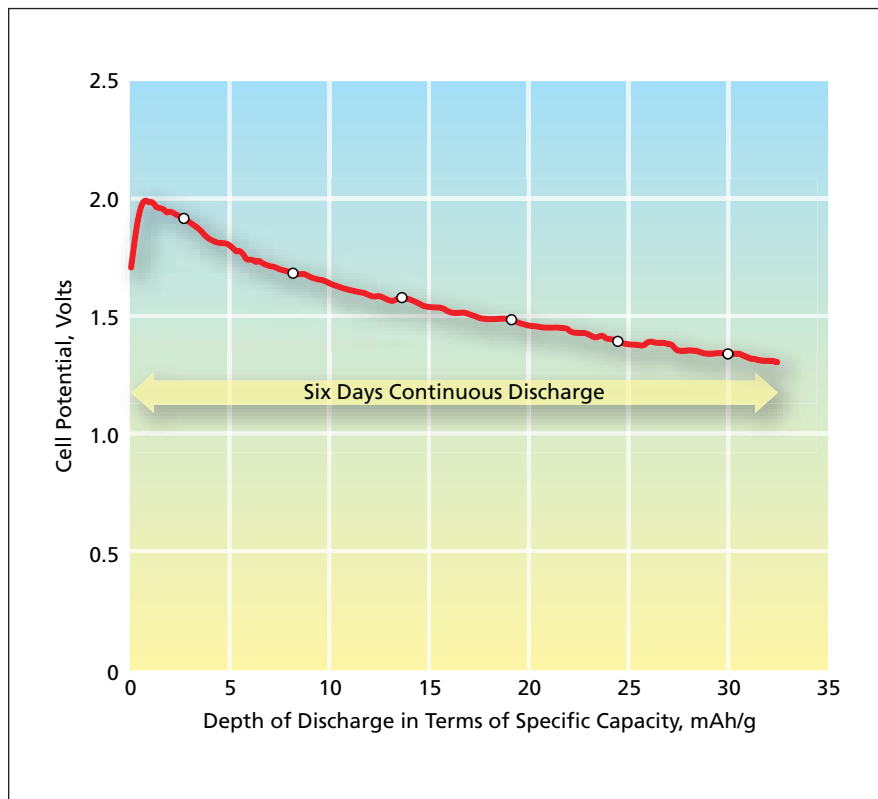
At the negative electrode (anode):



At the positive electrode (cathode):



One of the advantages of the NiF<sub>2</sub>/NaF:CaF<sub>2</sub>/Ca material system is that at high temperature, the solid electrolyte material is a conductor of fluoride ions (F<sup>-</sup>). Homogenous doping of CaF<sub>2</sub> with NaF or another aliovalent fluoride salt induces fluoride vacancies and



This Discharge Plot represents the performance of an NiF<sub>2</sub>/NaF:CaF<sub>2</sub>/Ca cell tested at a temperature of 450 °C for six days at a current density of 62.5 μA/cm<sup>2</sup>. While this discharge current density is comparatively low, further optimization in cell design is anticipated to enhance performance.

thereby sharply increases ionic conductivity. The electrolyte material can also be heterogeneously doped with ceria, zirconia, or alumina to further enhance fluoride conductivity. By means of a combination of homogenous and heterogeneous doping, the fluoride conductivity can be enhanced several orders of magnitude relative to that of pure CaF<sub>2</sub>, yielding a fluoride conductivity of 12.6 mS/cm at 440 °C — on a par with conductivities of Li-ion battery electrolytes at room temperature.

Unlike the active electrode materials in Li<sup>-</sup> anode/FeS<sub>2</sub><sup>-</sup> cathode cells, the active electrode materials in the present NiF<sub>2</sub>/NaF:CaF<sub>2</sub>/Ca cells exhibit negligible solubility in the solid electrolyte material. As a consequence, corrosion of the electrodes and self-discharge of the cell are greatly reduced.

To increase the ionic conductivity of the cathode of an NiF<sub>2</sub>/NaF:CaF<sub>2</sub>/Ca cell, in fabricating the cathode, one adds between 20 and 30 weight percent of the electrolyte material to the active cathode material. Similarly, to increase the electronic conductivity, one adds between 10 and 20 weight percent of graphite. The cathode structure as described thus far is then sintered. The cathode discharge reaction produces Ni, which enhances the electronic conductivity of the cathode. The corrosion resistance of Ni in fluorides in the absence of water is excellent. It has been conjectured that CuF<sub>2</sub> could be substituted for NiF<sub>2</sub> as the active cathode material, in which case the cathode reaction product would be Cu, which would enhance the electronic conductivity of the cathode.

The anode of an  $\text{NiF}_2/\text{NaF}:\text{CaF}_2/\text{Ca}$  cell consists of a solid Ca metal layer formed by pressing dendritic Ca into a disk shape and roughening the surface to enhance contact with the cathode/electrolyte/graphite. The conversion of the active anode material (Ca) to the main ingredient ( $\text{CaF}_2$ ) of the electrolyte material during discharge is fortuitous in that the accumulation of this material facilitates further discharge, unlike in most other electrochemical power cells, wherein accumulation of discharge products hinders further discharge. Ideally, the anode would be fabricated as a Ca

alloy containing approximately 5 mole percent of Na to form the desired NaF dopant for the  $\text{CaF}_2$  electrolyte as the cell discharges. At 450 °C, this alloy would remain a solid solution.

Several  $\text{NiF}_2/\text{NaF}:\text{CaF}_2/\text{Ca}$  cells have been fabricated and tested. The figure presents results from one such test. For testing purposes, these cells have been treated as primary (non-rechargeable) cells, but it is possible that these cells are rechargeable. If further tests confirm that they are rechargeable, then some of the cost and risk associated with manufacture and use of high-temperature batteries

could be reduced: Before being installed for use, batteries could be heated to operating temperatures; charged and discharged several times to verify that their voltages, capacities, and discharge-rate capabilities are as expected; then recharged; and finally cooled. In contrast, the voltages, capacities, and discharge-rate capabilities of non-rechargeable batteries cannot be verified prior to final use.

*This work was done by William West, Jay Whitacre, and Linda Del Castillo of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1), NPO-44643*

## Critical Coupling Between Optical Fibers and WGM Resonators

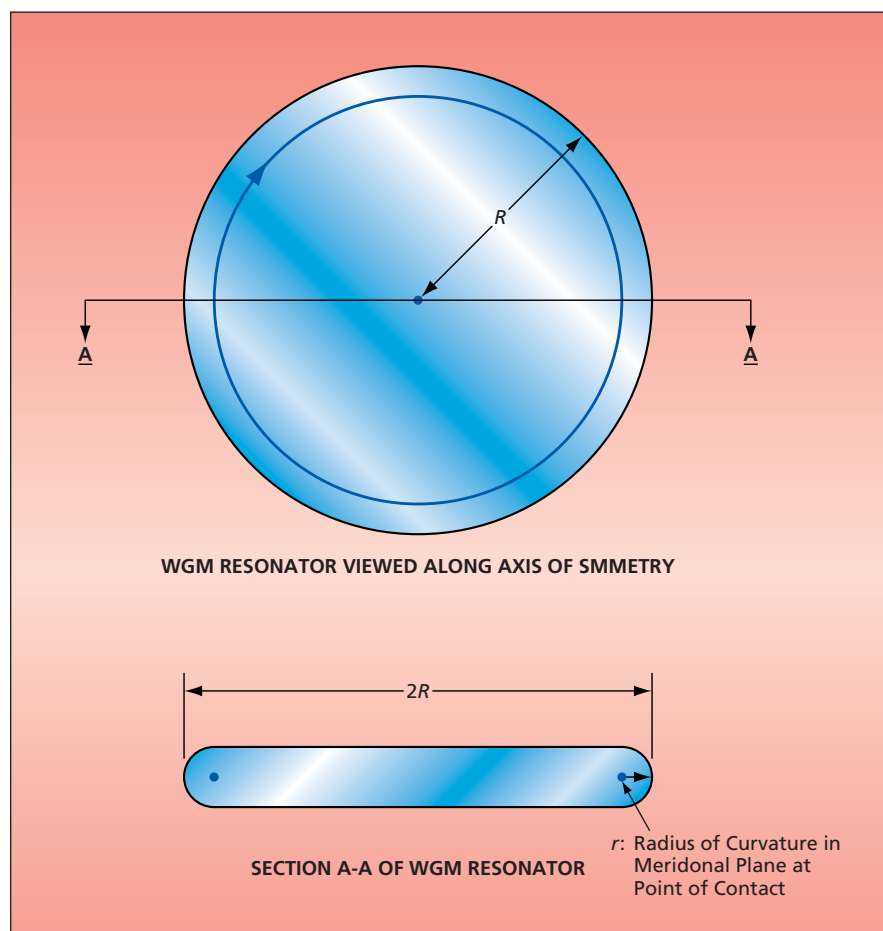
Recipes address issues of phase matching, aperture matching, and suppressing intermodal coupling.

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Two recipes for ensuring critical coupling between a single-mode optical fiber and a whispering-gallery-mode (WGM) optical resonator have been devised. The recipes provide for phase matching and aperture matching, both of which are necessary for efficient coupling. There is also a provision for suppressing intermodal coupling, which is detrimental because it drains energy from desired modes into undesired ones.

According to one recipe, the tip of the single-mode optical fiber is either tapered in diameter or tapered in effective diameter by virtue of being cleaved at an oblique angle. The effective index of refraction and the phase velocity at a given position along the taper depend on the diameter (or effective diameter) and the index of refraction of the bulk fiber material. As the diameter (or effective diameter) decreases with decreasing distance from the tip, the effective index of refraction also decreases. Critical coupling and phase matching can be achieved by placing the optical fiber and the resonator in contact at the proper point along the taper. This recipe is subject to the limitation that the attainable effective index of refraction lies between the indices of refraction of the bulk fiber material and the atmosphere or vacuum to which the resonator and fiber are exposed.

The other recipe involves a refinement of the previously developed technique of prism coupling, in which the light beam from the optical fiber is collimated and focused onto one surface of a prism that has an index of refrac-



A Typical Whispering-Gallery-Mode Resonator is characterized by, among other parameters, radii of curvature  $r$  and  $R$  that appear in the equations that describe the conditions for critical coupling.

tion greater than that of the resonator. Another surface of the prism is placed in contact with the resonator. The various components are arranged so that

the collimated beam is focused at the prism/resonator contact spot. The recipe includes the following additional provisions: