

# Advanced Thin Film Sodium Sulfur Battery

## Abstract

Ford Motor Company invented the Sodium-Sulfur (NaS) Battery in 1966 with the promise of higher energy density for use in electric vehicles. The major stumbling block to adoption was the battery's high operating temperature (300-350 °C); and over forty years later, the only company producing NaS batteries commercially is a Japanese firm and the only application is large scale energy storage. Trans Ionics Corporation through its subsidiary, Natrium Energy Corporation, is developing an Advanced Thin Film Sodium Sulfur (NaS) Battery Module that incorporates innovative technologies offering the following benefits in EV and PHEV applications:

- Reduction of 25-50 % in size/weight vs existing NaS batteries
- Operation at 25 – 100 °C versus ~350 °C
- Increased energy density and more flexible battery design via a planar cell architecture
- Battery cost at least as low as Sodium Metal Halide or Lithium Sulfur

## 1. The Sodium-Sulfur Battery

### 1.1. Background

A NaS battery is a type of molten metal battery constructed utilizing elemental sodium (Na) and elemental sulfur (S) as electrodes. This type of battery has been demonstrated to have a high energy density, high efficiency of charge/discharge (89–92%), long cycle life and is fabricated from inexpensive materials. However, because of its high operating temperatures (300 to 350 °C) and the highly corrosive nature of the sodium polysulfides, such cells are primarily suitable for large-scale, non-mobile applications, such as grid energy storage.

Sodium-sulfur battery technology has been the focus of research now for over four decades; and interestingly, the original work by Ford was directed to the production of a higher energy density battery for electric vehicles. Until 1997, both Ford and GM had electric vehicles in various stages of testing. The Ford Ecostar van was powered by a 30 kWhr (at 80% depth of discharge) sodium-sulfur battery, while the GM vehicle was powered by a nickel metal hydride (NiMH) battery; but, unlike the NiMH battery, the NaS battery has yet to find an automotive application in the U. S. that is economically viable; and work by Ford has essentially been terminated.

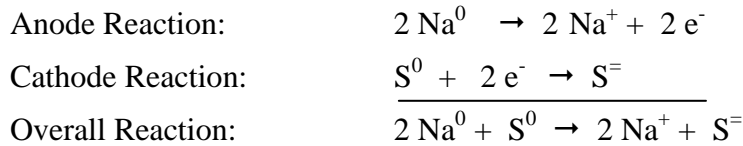
Commercialization of this form of the NaS battery in small to intermediate power markets (< 50 kW) seemed to fail due to the extreme temperatures required and the safety issues incurred with potential rupture of cells in (for instance) an automobile accident. So the only market left was large scale load-leveling batteries for stationary power plants; and there are currently no U. S. companies that offer these products. As a result, companies like American Electric Power have had to team up with NGK Insulators of Japan to install a 1 MW load leveling facility in West Virginia; and the 80 ton, 2 semi-trailer sized battery is expected to have 7.2 MWh of capacity at the charge and discharge

rate of 1 MW. Xcel Energy has announced that it will be testing a wind farm energy storage battery based on 20-50 kW sodium-sulfur batteries, also from NGK.

### 1.2. Conventional NaS Battery

A conventional NaS battery has three components: (1) an anode compartment, (2) a solid electrolyte and (3) a cathode compartment. Sodium Beta Alumina ( $\beta''\text{-Al}_2\text{O}_3$ ) is the electrolyte of choice. This solid electrolyte is permeable only to sodium ions ( $\text{Na}^+$ ) and prevents the other cell components (sodium and sulfur-rich sodium polysulfides) from coming into physical contact.

Under normal discharge conditions, sodium metal is oxidized to sodium ions ( $\text{Na}^+$ ), which diffuse across the solid electrolyte and combine with sulfur (which has been simultaneously reduced to  $\text{S}^-$ ) producing a distribution of sodium polysulfides and electricity at  $\sim 2$  V. The electrochemical reactions of the discharge cycle are well-understood and can be described as shown below:



Sodium metal melts at 98 °C and sodium polysulfides have even higher melting points; so in order to provide the ionic mobility necessary for high power density, the system must be maintained as a molten salt, which requires a battery operating temperature in the range 300 – 350 °C. As a precaution against mechanical breakage, electrolytes in the past have been fairly thick (averaging 1-2 mm in thickness).

So, the two major problems with sodium-sulfur batteries to date have been (1) the requirement to operate at high temperatures, which is, in part, caused by the thickness of the electrolyte and in part caused by the high viscosity of a molten salt system, and (2) their weight.

### 1.3. Advanced Thin Film NaS Battery

The NaS battery under development by Trans Ionics overcomes these problems by (1) significantly reducing the thickness of the electrolyte and (2) operating with a proprietary mixture of components in the anode and cathode sections both of which permit operation at far lower temperatures than previously thought possible for NaS batteries.

The effect of electrolyte thickness can be appreciated by evaluating its effect on Area Specific Resistance (ASR) for a NaS battery as shown in the table below. Ionic conductivities (S/cm) were determined experimentally by impedance spectroscopy.

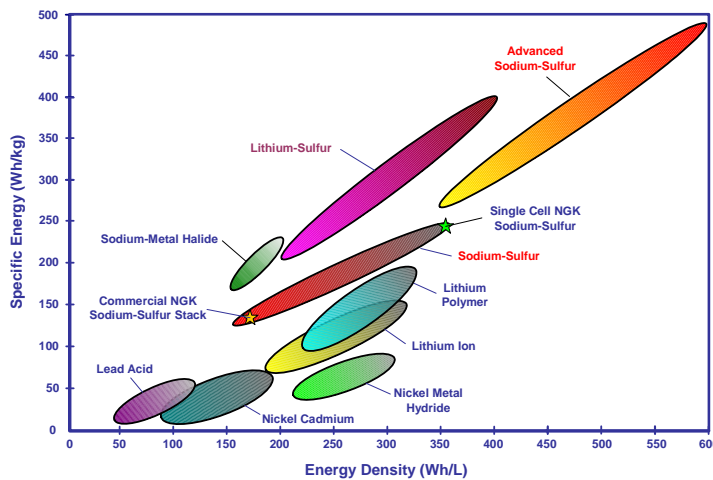
Temperature (°C)	350		25	
	Ford	TIC	Ford	TIC
Thickness (cm)	0.100	0.0005	0.100	0.0005
Conductivity (S/cm)	0.246	0.246	0.004	0.004
Area Specific Resistance ( $\Omega \text{ cm}^2$ )	0.406	0.002	24.82	0.124
Voltage drop @ 7.5 kA/m <sup>2</sup> (V)	0.304	0.002	18.62	0.093

As can be seen, reducing the thickness of the electrolyte layer to 5  $\mu$  (from 1,000  $\mu$ ) results in a drop in ASR of a factor of 200 over the conventional NaS battery. With the other improvements proposed, this allows operation at 25 °C with a voltage drop of only 0.09 V. Even if the conventional battery could be operated at 25 °C, the resulting 18.6 V loss would render it inoperable. So the first advancement is an ultrathin solid electrolyte.

The second advancement is the development of a mixture of components that facilitate operation of a NaS battery at lower temperatures. While they are proprietary, it can be said that they involve the use of liquid species that enhance the solubility and conductivity of both the sodium polysulfide cathode and the sodium anode thus eliminating the need to run as molten salts at elevated temperatures.

## 2. State of the Art in Batteries for Electric Vehicles

Rechargeable batteries can have a wide range of energy densities as shown in the figure. Of the batteries under serious consideration for electric vehicles, lithium ion and lithium polymer batteries are the most advanced but are still limited to system level Specific

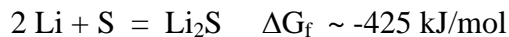


Energies of <160 Wh/kg. Sodium metal halide batteries are under development by GE but operate at 290-350 °C and contain very thick electrolytes like the NGK system.

The highest Specific Energy and Energy Density is demonstrated by alkali metal sulfur batteries: lithium-sulfur (LiS) and sodium-sulfur (NaS); and these will be the focus of the balance of this review.

### 2.1. Advantages of Alkali Metal Sulfur Batteries

Alkali Sulfur (like Li-S or Na-S) batteries have high theoretical Specific Energies because each sulfur ion can accept two metal ions as shown below for lithium.



Because of the very low molecular weight of Li, the large negative Gibbs free energy of formation converts directly to a *theoretical* Specific Energy of ~ 2,500 Wh/kg or more than four times that of a Li ion battery.

Sodium has a higher molecular weight than Li and the formation of Na<sub>2</sub>S has a lower free energy of formation (~ -350 kJ/mol). Nevertheless, the battery still has a theoretical Specific Energy of ~ 1,250 Wh/kg or still twice that of the Li ion battery.

There are two major issues with LiS cells as they currently exist: (1) development of rough lithium surface morphology and (2) Li/liquid electrolyte depletion. In the first case, dissolution and redeposit of Li over a number of charging and discharging cycles creates (a) dendrites extending from the surface which can pass through the porous polymeric separator and short out the cell or (b) porous “mossy” lithium deposits which can absorb

electrolyte leading to premature anode disintegration. In the second case, loss of solvent due to reaction with Li prevents proper operation of the cathode; and the reaction products increase cell impedance.

The proposed advanced thin film NaS battery contains a solid (not a liquid) electrolyte that does not exhibit either of these problems.

### **3. Technical Requirements**

As stated previously, the theoretical Specific Energy of the NaS reaction is 1,250 Wh/kg. Unit cells from commercial NaS batteries sold by NGK exhibit 367 Wh/L and 222 Wh/kg which are limited by electrolyte thickness and cell resistance. Unfortunately, these values are reduced to 160 Wh/L and 118 Wh/kg (only 9.4 % of theoretical capacity) when the system is assembled due to the difficulty of running at 350 °C.

The proposed thin film NaS battery will decrease the thickness of the electrolyte by a factor of 200 and allow the system to operate efficiently at 25 °C. The unit cell is expected to exhibit at least 600 Wh/L and 475 Wh/kg and the full cell is expected to show at least 300 Wh/L and 300 Wh/kg (for 24% of theoretical capacity).

Key technical risks are (1) producing a 5 μ thick electrolyte that is pinhole-free, (2) determining the optimum composition for the anode and cathode fluids to minimize resistance and (3) utilizing the lightest components possible for the cell to minimize the weight. The technology is currently at TRL-3 for the electrolyte and TRL-2 for the electrodes; however, we believe that with appropriate funding, the technology can achieve TRL-6 within 24 months.

### **4. Manufacturing Process and Scalability**

The Ford and NGK processes use electrophoretic deposition of β"-Al<sub>2</sub>O<sub>3</sub> onto stainless mandrels to form the electrolytes. Because these were stand-alone electrolyte tubes, they had to be thicker to protect against catastrophic rupture. The proposed process uses tape casting to produce a microporous substrate and screen printing or other techniques (depending on the desired thickness) to apply the dense electrolyte. Because these batteries will be operated at 25-100 °C, conventional, flexible epoxy seals are planned and materials of construction can and will include plastic as well as thin metallic components that are both lightweight and cost effective.

### **5. Impact on US Leadership in Battery Technology Development/Manufacturing**

NaS batteries were invented in the U. S. but have never been commercially produced outside of Japan. Success of the current project will create a battery manufacturing organization that can compete effectively not only in the smaller EV market but also in the wind and solar power storage markets which are served almost exclusively by NGK. This impacts security of the US in decreasing consumption of petroleum supplied by Middle Eastern nations and creates/maintains jobs in the US to provide in the pursuit of clean, stable power sources.