UNIVERSITY OF FLORIDA

An Integrated Sustainable Transportation System

PI: Eric Wachsman **Co-PI:** Shirley Meng
Students: Dong Jo Oh (PhD), Eric Armstrong (PhD), Kang Taek Lee (PhD), Byung Wook Lee (PhD), Nick Vito (PhD), and Christopher R. Fell (PhD)

Description: The proposed vehicle, operating on biofuel while in transit and charged by the sun while parked, is the ultimate sustainable transportation system operating completely on renewable American energy resources. Moreover, the use of solid oxide fuel cells (SOFCs) rather than an IC engine in this hybrid vehicle results in a dramatic improvement in efficiency and reduction in emissions. SOFCs are the most efficient technology for converting energy from hydrocarbon fuels to electricity on a "well to wheels" basis. In contrast, the more conventional fuel cells require hydrocarbon fuels to first be converted to H_2, with resultant efficiency losses, followed by losses due to H_2 transport and storage. Therefore, on a system-basis SOFCs hold the potential for producing the least CO_2/kWh from conventional fuels, and if designed to operate on biofuel would in effect be carbon neutral and operating on a renewable resource. *If developed this vehicle would be a transformational change in transportation technology*.

Budget: $594,000

Universities: UF

External Collaborators: Solid-State Energy Technology, Inc., Lynntech, Inc., Planar Energy Devices, Inc., CFX Battery, Inc.

Progress Summary

Anode Supported Cell Development

For high performance SOFCs at lower temperature operation, a simple method was developed to dramatically improve anode functional layer (AFL) performance by dispersion of nano-precursors into a conventional colloidally-deposited AFL. (Fig 1) The composition used for the anode substrate, the colloidal AFL, and the nano-precursor integrated into the AFL was Ni and Gd-doped ceria (GDC). The electrolyte composition was GDC, a system that has received much attention for its potential use for IT-SOFCs. The novel AFL exhibited over 1.3 W/cm^2 at 650 °C—a 107% increase in maximum power density compared a similar cell with no AFL and a 26% increase for a cell with a colloidal AFL. (Fig 2) This AFL can be applied on various anode-supported SOFCs, such as the ESB/GDC bilayered electrolyte cell. Due to the simple fabrication procedure, this AFL can be easily applied to large planar cells for stack cell fabrication.

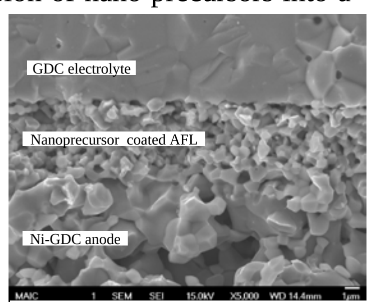

Figure 1. SEM image of cross sectional SOFC structure with novel AFL.

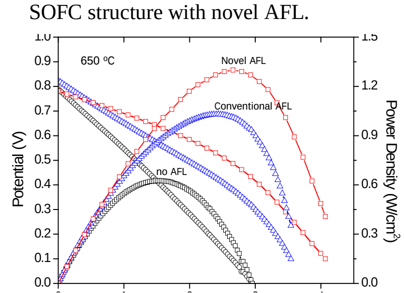

Figure 2. Performance of novel AFL compared to colloidal AFL and no AFL at 650 °C (30 sccm of H_2/Air.

Further studies are being done to optimize performance in relation to microsturcture and AFL composition using a dual beam focus ion beam / scanning electron microscope (FIB/SEM). Initial results show that a NiO to GDC ratio of 6 to 4 yields the highest triple phase boundary density of ~10 / μm^2 along with the highest maximum power density in the study. A 3D reconstruction of the anode and colloidal AFL are shown side by side in figure 3.

Cathode Development

A high performance cathode was developed with one of the lowest reported area specific resistances (ASR) ever reported, especially at the low temperature range of 500 – 600 °C. The cathode is a composite composed of stabilized bismuth oxide as an ionic conductor and nano-sized high-temperature pyrochlore bismuth ruthenate as an electronic conductor. The nano-sized bismuth ruthenate was successfully synthesized for the first time using the glycine-nitrate combustion (GNC) method, enabling a further decrease in activation polarization losses by expanding specific surface area for oxygen reduction.

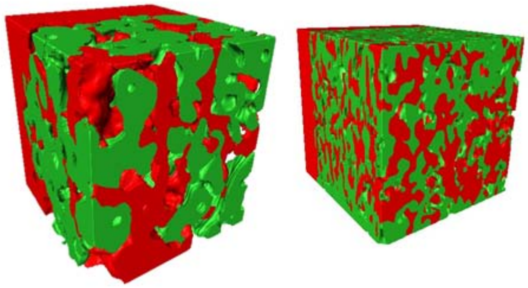

Figure 3. Bulk anode (left) and colloidal AFL (right) reconstructions—GDC (red) and Ni (green)

Initial results also show a unique behavior in the 500 – 600 °C temperature range where resistance decreases with decreasing temperature, supposedly related to metallic behavior from the coating of bismuth ruthenate nanoparticles. (Fig 4) Other synthesis methods such as amorphous citrate, Pechini type, and polymerized complex methods failed to create high purity bismuth ruthenate nanoparticles due to the lower synthesis temperature and longer reaction time.

Energy storage in the integrated sustainable transportation system

$LiMn_2O_4$ spinel material is an attractive compound as a cathode material in lithium-ion batteries, due to its economical and environment advantages over $LiCoO_2$. However, $LiMn_2O_4$ tends to exhibit capacity fade in the 4V region, particularly at elevated temperatures. Factors such as manganese dissolution into the electrolyte and development of micro-strain during cycling have been suggested to be the main sources of capacity fade. The poor cycling performance could be improved by partial substitution of manganese with other metals, an approach of making the $LiM_xMn_{2-X}O_4$ (M = Co, Mg, Cr, Ni, Fe, Al, Ti, Cu, Zn etc.) electrode materials. It has been found a high voltage plateau that can be achieved in spinel materials accompanies the transition metal doping. Among all $LiM_xMn_{2-X}O_4$ materials, $LiNi_{0.5}Mn_{1.5}O_4$ is an attractive high voltage cathode material since it offers a flat voltage plateau at 4.7 V and demonstrates a reversible capacity >135mAh/g. First principles computation based on density functional theory (DFT) is used to examine the voltage profile and electronic structures of the $LiM_xMn_{2-x}O_4$ (M =, Cr, Fe, Co, Ni, Cu,).The Li diffusion activation barriers in each material are also calculated and compared. The computation results suggest that $LiM_{1/2}Mn_{3/2}O_4$ spinel can have quite different activation barrier for Li diffusion depending on the doping elements, and doping with Cu and/or Co can potentially lower Li diffusion barrier compared with Ni doping. Our experimental research was focused on $LiNi_xCu_yMn_{2-x-y}O_4$ ($0<x<0.5$, $0<y<0.5$). Previous studies show that the Cu-rich spinel electrodes are significantly more stable during electrochemical cycling than the Ni-rich electrodes. The $LiNi_xCu_yMn_{2-x-y}O_4$ oxide materials have the potential to achieve high rate, high voltage, high discharge capacity and excellent cycling performance. In order to systematically study the composition, crystal structure, electronic structure and electrochemical property relations of the spinel oxide, $LiNi_xCu_yMn_{2-x-y}O_4$ ($0<x<0.5$, $0<y<0.5$) are experimentally synthesized by sol-gel method. We have found that the amount of Cu will affect the lattice parameters, the cation disorder in the spinel lattice, the particle morphology and electrochemical properties. Although the reversible discharge capacity decreases with increasing Cu amount, optimized materials such as $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ exhibits high capacities at high rates. (See Figure 4.)

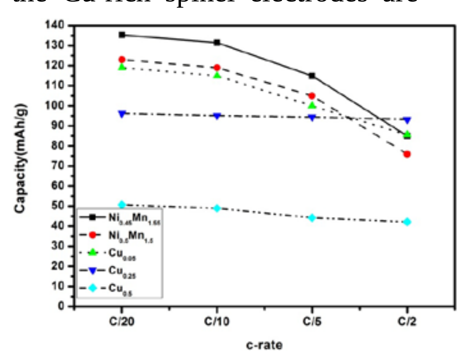

Figure 4: Rate Capability of $LiNi_xCu_yMn_{2-x-y}O_4$