A Review of the Center for Fluorinated Functional Materials

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ABSTRACT

Center for Fluorinated Functional Materials was established in July 2017 with strong support from the State of South Dakota. The mission of this R&D center is to build a self-sustained discovery-based research center that boosts the South Dakota economy through commercialization of fluorinated functional materials in the sectors of materials and advanced manufacturing, energy and environment, and human health and nutrition. The creation of this research center is expected to overcome two significant challenges in transforming the South Dakota economy to a knowledge-based economy: 1) discovery of innovative technology and 2) building a technology- and business-capable team. The R&D center integrates research and commercialization with focus on innovations in fluorinated functional materials. Five highly competitive research and innovation focuses include 1) photonic materials, 2) semiconductor materials, 3) high capacity energy storage materials, 4) catalysis, and 5) sensors. The center assembles necessary expertise to tackle these challenges for the State of South Dakota by tightly integrating discovery-based research, technology transfer, and workforce development. In this presentation, we will brief introduce these five technical focus areas with emphasis on high capacity energy storage materials that can reach 1000 mAh/g specific capacity when used in cathode.

Keywords: fluorinated materials, finger printing technology, energy storage, photonic materials, catalysis, sensors

INTRODUCTION

The creation of this R&D center addresses the critical needs for growing the South Dakota economy by directly targeting a key industrial sector, Materials and Advanced Manufacturing by focusing on unique fluorinated functional materials with a highly qualified team. As demonstrated in the following introduction section, the usefulness and uniqueness of fluorinated functional materials decides that this research center is like no other, not only in the state of South Dakota, but also in the nation among the academic setting. The immediate goal of this research center is to integrate discovery-based research and innovation with industries through technology transfer in fluorinated functional materials. Many examples in the history of science and technology evolution underpin the notion that discovery-based and hypothesis-driven research is the key to the technological innovation, from ancient pain killer medicine obtained from willow bark to the discovery of Teflon™, a fluorinated materials widely used in our daily life (for example, in non-sticky pans in our kitchen). The central theme of this research center for fluorinated functional materials is "from discovery to commercialization", a perfect pathway to boost the economy through innovation.

Given the broad range of applications of fluorinated functional materials, the outcome of this research center will further benefit other sectors, including energy and environment and human health and nutrition. Producing highly valued fluorinated functional materials in a high tech laboratory setting fits perfectly in the existing and growing industrial infrastructure. Fluorinated functional materials are widely used across all aspects of human activities, ranging from our daily life, non-sticky pans in our home, medicine for curing diseases, agriculture chemicals safeguarding our foodsupplies, ^{18}F radioactive isotope labeled pharmaceuticals for cancer diagnosis and treatment monitoring, to high-tech applications including high performance chips for supercomputing and robotic applications, high performance lubricants for aerospace applications, large scale lithium batteries for new electrical automobiles.

The economic impact of fluorinated functional materials is significant. Here just a few examples: Lipitor, one of the many fluorinated drugs, was the 2008's best-selling drug and had a $5.9 billion revenue that year; every single smart phone has a lithium battery containing fluorinated electrolytes; metal fluorides and fluorinated polymer films are the choice for optical coating materials, having an estimated $6.5 billion market value in 2013 with a growth rate of 6.5% annually. It is our team's vision to bring this high tech, high value, and high profit fluorinated functional material industry to the State of South Dakota. One important thing we must point out here is that, in order to boost the South Dakota's economy, it requires much needed knowledge-based economy with less infrastructure investment, but high margin return with products that only requires small scale production. This is the key to take off the South Dakota knowledge-based economy. This research center strategically focuses on this target: the production of highly profitable product with less infrastructure investiment.

TECHNOLOGY INVENTION

In this section, we will describe five tasks and corresponding innovations: 1) fluorinated flexible electronic and optoelectronic materials; 2) fluorinated photonic materials; 3) fluorinated battery materials; 4) fluorinated catalytic materials; and 5) fluorinated sensing materials.

Significant efforts have been made to develop organic electronics and optoelectronics with an ultimate goal of being flexible.[1-11] Despite the great progress in organic electronics and optoelectronic research, many practical applications of organic electronics and optoelectronics remain unrealized, particularly on flexible electronic and optoelectronic devices, including, for example, wearable sensor arrays for patient health condition monitoring and reporting system. One big problem is that moisture and oxygen significantly reduce both the stability and the efficiency of current flexible electronics and optoelectronics made with hydrocarbon-based organic semiconductor materials which are thermally and photochemically unstable. Inorganic barrier coatings stabilize the devices but at the expense of flexibility. Fluorinated organic semiconductor materials provide the solution of choice for the next generation of flexible electronics and optoelectronics because of **1)** its robust thermal and photochemical stability; **2)** its superhydrophobicity which prevents moisture permeation; and **3)** ease of tuning electronic and optical properties through various degrees of fluorination.

Our recent work developed both fluorinated small molecules and polymeric organic semicondctor materials. In particular, the center has discovered a large area free standing ultra-thin fluorinated polymeric films that has thickness less than 10 nm. **Figure 1** shows a SEM image of ultra-thin film developed in our lab by a simple and scalable interfacial synthetic method. This fluorinated porous polymer film possesses many advantages for various applications. For example, by adjusting the size and the shape of the monomers, the pore size of polymer thin film can be easily ajusted as needed, which is very important for seperation technology. Another potential application for this thin film is flexible electronics and optoelectronics as we are integrating large conjugated aromatics into the thin film. Such effort is ongoing within the center. The center is actively looking for industrial partner (s) to commercialize this thin film technology through licensing-based tech transfer.

Fluorinated photonic materials is another area that currently involved in both research and commercialization activities of the center. The key technologies related to the fluorinated photonic materials are security printing and ultra-sensititve finger print identification without damaging the DNA sample associated with the finger print. We have made significant advances in the design and use of fluorinated photonic materials and surface modifications for the control physico-chemistry properties of these materials,[12-15] which have applications in chemical sensing, photovoltaics, security printing, and anti-counterfeiting technologies [12-13, 16-22]

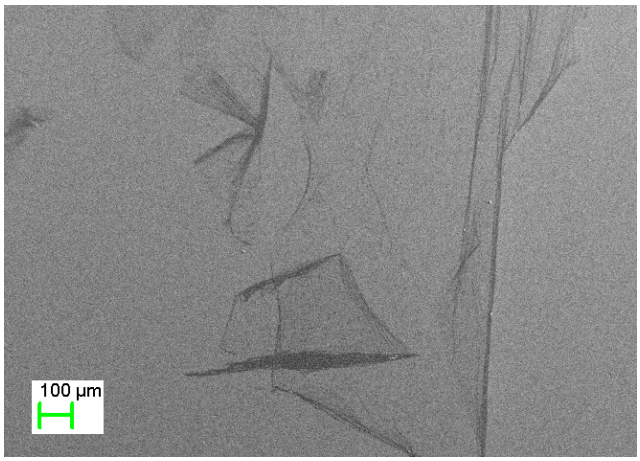

Figure 1: SEM image of large area ultra-thin fluorinated porous film prepared at the interface. The film was captured on a silcon wafer for SEM imaging.

Our fluorinated battery material project is developing high capacity cathodic materials which is significantly important for battery applications. The low capacity cathodic materials used in current lithium ion batteries is a bottle-neck for developing the next generation high capcaity batteries.[23-31] The heavy transition metal elements limits the capacity of transition metal oxide based cathode below 300 mAh/g. High capacity sulfur based cathode often faces stability problem due to high solubility of LiS_x in organic electrolyte solutions. Carbon fluoride, CF_x ($0<x<1.3$, with most cases $x\leq1.0$), is a high capacity cathodic material that suffers from low discharging rates.[32] Preparation of CF_x materials requires high temperature direct fluorination of graphite with F_2 gas which the procedure itself possesses significant safety threat and quality control challenges.

We have discovered a new type of fluorinated carbon materials that shares similar composition with the traditional carbon fluoride cathodic materials but with safer proparation method in a regualr laboratory setting (without using the dangoues F_2 gas!). The material itself possesses 1) high capacity up to 1,000 mAh/g; 2) high conductivity which traditional conductive carbon black is no longer needed; 3) higher diacharge rate capability; and 4) better mechanical properties. The preparation of these new fluorinated caron materials can be done at various scales in the laboratory without compromising the production yield.

This new type of fluorinated carbon materials can be directly used as cathodic materials without conductive

additive (e.g. carbon black) and mechanical binder (e.g. PVDF) which are normally 15-20% of the total mass of cathode on Al current collector. This results in about 15% capacity increase for the cathode when our new fluorinated carbon materials are employed in the cathode. Our initial test of this material shows discharge capacity reach to 1,000 mAh/g at 0.5 C discahrge rate. The initial discharge voltage is around 1.4 V, however, the dischage voltage increase to 2.1 V after an initial polarization treatment, giving a very stable discharge plateau all the way to the end of discahrge process. Our initial charging results show that the overpotential is still quite high. Searching and optimizing the charging conditions is currently underway to reduce the overpotential for the charging process.

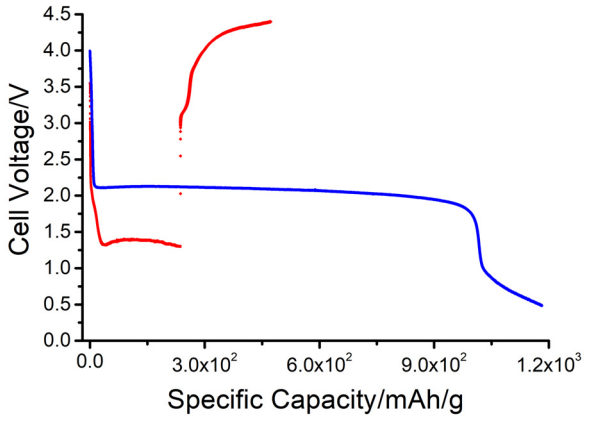

Figure 2: Discharge and charge behaviors of the new fluorinated carbon materials. Red line, initial discharge and charge profile at 0.5 C rate. Blue line, complete discharge profile at 0.5 C rate after initial polarization treatment. Anode: lithium foil, cathode: new fluorinated carbon materials, electrolyte 1.0 M $LiPF_6$ PC solution.

In addition to organic semiconductor materials, batteries, and finger print technology, the center also develops catalytic fluoriantion reactions, fluorinated molecular sensors, and surface-enhanced Raman spectroscopic method for detecting fluorinated compounds in the enviroment. In summary, the Center for Fluorinated Functional Materials advances many R&D areas for new materials and related products. We expect that this collective effort on fluorinated functional materials will soon drive the innovations from laboratory to the market.

COMMERCIALIZATION

The center is actively seeking industrial paternarship with companies through paternarship, technology licensing, and R&D sponsorship. South Dakota is a business friendly state with low cost living. We welcome interesting parties to contact the University of South Dakota Tech Transfer Office at TTO@usd.edu or the center director Dr. Haoran Sun at Haoran.Sun@usd.edu for more detailed information on R&D projects and technology transfer.

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