ORNL/TM-2014/250

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Chemical Sciences Division

Neutron Scattering Studies of Liquid on or Confined in Nano- and Mesoporous Carbons, Including Carbide-Derived Carbons

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ABSTRACT

This project involved the synthesis of microporous graphitic-carbon powders with subnanometer average pore size, and very narrow pore size distributions, and the use of these materials in experimental studies of pore-fluid structure and dynamics. Samples of carbide-derived carbon powder, synthesized by extraction of the metal cations from TiC by a high temperature chlorination process, followed by high temperature vacuum annealing, were prepared by Ranjan Dash and his associates at CRADA partner Y-Carbon, Inc. The resulting material had average pore sizes ranging from 5 to 8 Å. These powders were used in two experiments conducted by researchers involved in the Energy Frontier Research Center Directed by David J. Wesolowski at ORNL, the Fluid Interface Reactions, Structures and Transport (FIRST) Center. FIRST-funded researchers at Drexel University collaborated with scientists at the Paul Scherrer Institute, Switzerland, to measure the expansion and contraction of the microporous carbon particles during charging and discharging of supercapactor electrodes composed of these particles (Hantell et al., 2011, *Electrochemistry Communications*, v. 13, pp. 1221-1224.) in an electrolyte composed of tetraethylammonium tetrafluoroborate dissolved in acetonitrile. In the second experiment, researchers at Oak Ridge National Laboratory and Drexel University conducted quasielastic neutron scattering studies of the diffusional dynamics of water imbibed into the micropores of the same material (Chathoth et al., 2011, *EuroPhysics Journal*, v. 95, pp. 56001/1-6). These studies helped to establish the role of pores approaching the size of the solvent and dissolved ions in altering diffusional dynamics, ion transport and physical response of conducting substrates to ion desolvation and entry into subnamometer pores.

STATEMENT OF OBJECTIVES

The objective of this CRADA was to achieve fundamental understanding of the structure and dynamics of various fluids in contact with and/or confined in nanoporous carbide derived carbons (CDCs), by using neutron scattering and other probes of fluid transport and dynamics. Y-Carbon, our industrial partner, wanted to produce CDC material that would enable us to probe the ultimate pore size limits of solvent and ion incorporation into materials that are being widely used in supercapacitors and various chemical separations processes. ORNL partners needed carbon materials with extremely small, monodisperse pore sizes not readily available elsewhere.

BENEFITS TO THE FUNDING DOE OFFICE'S MISSION

The FIRST Energy Frontier Research Center, funded by DOE's Office of Basic Energy Sciences, seeks to develop fundamental understanding, and validated predictive models of the unique nanoscale environment at fluid-solid interfaces found in nature and a myriad of applications, including electrical energy storage and catalysis. One of the central goals of the FIRST Center is to explore the behavior of fluids in pores so small that ions and even the solvent molecules of electrolytes like water and acetonitrile have difficulty physically squeezing into the pores and especially diffusing along the pores, driven by chemical and electrical potential gradients. The computational simulations developed in FIRST to predict the behavior of such electrolytes in charged and uncharged nanoporous materials must be be validated by experimental studies that isolate the critical variables, including pore size and pore surface properties. The CDC materials produced by Y-Carbon, Inc. were ideally and uniquely-suited to such studies.

TECHNICAL DISCUSSION OF WORK PERFORMED BY ALL PARTIES

Nanoporous CDC powders with a particle size of ~2 microns were produced by Y-Carbon staff. The pore size was controlled by chlorination temperature, using details described by Dash et al. (2006, *Carbon*, v. 44, pp. 2489-2497). This material was distributed to FIRST Center researchers at Drexel University (Professor Yury Gogotsi and associates) and ORNL (Wesolowski and Eugene Mamontov). The Drexel researchers teamed with scientists at the Paul Scherrer Institute, Switzerland to conduct in situ dilatometry studies of the swelling and contraction of CDC electrodes subjected to current-voltage cycling form -1.5 to + 1.5 volts. The chlorination temperature affected the final pore size of the CDC powders, with samples exhibiting average pore sizes of 5.8, 7.0 and 8.5 Å, at chlorination temperatures of 300, 600 and 800 °C (CDC-300, CDC-600 and CDC-800, respectively). The cyclic voltage was applied to the CDC electrodes immersed in 1 Molar tetraethylammonium borate in acetonitrile. Electrode swelling was observed that was reversible and exhibited hysteritical behavior with maximum response at the potential exteremes. Maximum swelling of 1.5 to 2.5 % was observed at -1.5 volts, near zero at zero applied external potential, and 0.75 to 1 % at +1.5 volts. The larger expansion of the negatively-charged electrode corresponded to marked narrowing of the CV curves during voltage cycling at 1 mV/s scan rate, indicating that the large tetraethylammonium cations were unable to fully access the subnanometer pores, and that cation injection produced more strain on the pore walls than did the smaller tetrafluoroborate anion in positively-charged pores. This is a significant result that impacts the design of supercapacitor electrodes, both in terms of the physical response of the electrodes to charge/discharge cycles, as well as the maximum power output of the electrode assembly. Details of this study are summarized in the publication by Hantell et al. (2011) listed in the abstract of this report.

The CDC-600 and CDC-800 materials were also used in quasielastic neutron scattering (QENS) studies conducted by FIRST researchers at ORNL's Spallation Neutron Source, using the BASIS backscattering spectrometer. Pure H_2O was drawn into the CDC subnanometer pores by exposing the powders to saturated H_2O vapor in a closed vacuum oven at 80 °C for 24 hours. Complete pore filling by water in these subnanometer pores was confirmed by other ORNL researchers, using small angle neutron scattering (He, et al., 2012, *Microporous and Mesoporous Materials*, v. 149, pp. 46-54). QENS spectra were taken at 10 degree intervals from 250 to 170 K, and were analyzed in terms of the characteristic relaxation times (tau) of water molecule diffusive motions. The temperature dependence of tau exhibits super-Arrhenious behavior that could be described by the Vogel-Fulcher-Tammann (VFT) law in the 250 – 190 K temperature range, with Arrhenius diffusion at lower temperatures. The temperature of the dynamic crossover between the two regimes in water confined in the 6-8 Å CDC pores is similar to that observed for water in hydrophobic confinement in much larger pores, such as 14 Å ordered mesoporous carbon and 16 Å double-wall carbon nanotubes. Thus, the dynamical behavior of water remains qualitatively unchanged enven in very small hydrophobic pores. Molecular simulations of water in graphene slit pores conducted by other FIRST Center researchers predicted water exclusion from perfectly hydrophobic pores less than 9 Å wide, suggesting that the cylindrical CDC pores may be less hydrophobic than graphene, due to surface curvature effects or defects in the pore walls. These studies indicate that it is possible to develop porous carbon electrode and membrane materials for capacitive electrical energy storage, water desalination and chemical separations that can operate at near-atomic level pore sizes. This research is summarized in the publication by Chathoth et al. (2011) listed in the abstract of this report.

SUBJECT INVENTIONS

No inventions were generated in the course of these studies.

COMMERCIALIZATION POSSIBILITIES

Our research, which has been published in the open scientific literature, may serve to aid in the design of commercial materials and processes, such at capacitive electrical energy storage and water desalination.

PLANS FOR FUTURE COLLABORATIONS

Shortly after the establishment of this CRADA agreement, Y-Carbon, Inc. switched their production lines to forms of carbon other than CDC, with larger pore sizes. Y-Carbon, Inc. went out of business through a bankruptcy process in 2013. As a result of these events, ORNL curtailed the full range of planned collaborative activities with the CRADA. Of the $75,000 budgetted for ORNL activities within the CRADA ($25,000/year for 3 years), only $20,143 were actually costed, and the remaining funds have been deobligated and returned to the FIRST Center budget for other activities. We do not anticipate any future collaborations associated with this CRADA.

CONCLUSIONS

Considering the short period of time involved before Y-Carbon changed it's product line, and the small amount of money spent on FIRST Center research, we consider this a highly successful CRADA activity, which resulted in two papers published in the peer-reviewed scientific literature that reported on the ultimate pore size limits of functionality of nanoporous carbon materials.