FIRST Center Research Perspective:

Onion-like carbons, their formation, properties, and performance

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Research Summary: We investigated the formation mechanism, and physical and electrochemical properties of a unique carbon allotrope, called onion-like carbon (OLC, US Patent 20,130,244,121, filed September 17, 2010, issued September 19, 2013). Using nanodiamond (ND) as a precursor, OLC was synthesized via vacuum annealing at various temperatures to better understand the kinetics of the transformation. Its high surface area, small particle size, and non-porous, exohedral structure allows OLC to be an attractive model system for both integrated computational and experimental probes of fluid-solid interface structures and dynamics, and the assembly of functional interfaces for capacitive and pseudocapacitive electrical energy storage. Our research focused on the electrochemical interface between the OLC surface and ions of an electrolyte, and more specifically, how the structure of the electric double layer (EDL) is influenced by the OLC curvature when compared to planar or porous systems. When used as a supercapacitor electrode material, OLC outperforms traditional porous carbons at ultra-fast charge-discharge rates, which is a result of its exohedral structure allowing for increased ion mobility.[1-4]

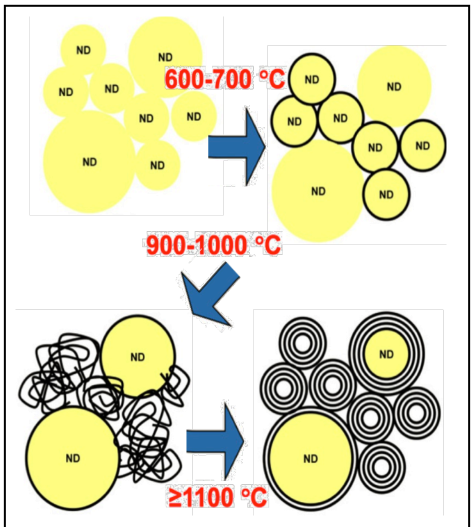

Figure 1. Details the progression of nanodiamond as it is transformed into OLC. The surface is initially graphitized, followed by a disordered phase at moderate temperatures, and finally complete transformation at the highest temperatures.[5]

Technical Details: OLC is synthesized from a nanodiamond precursor that is annealed in vacuum. For our studies of the formation mechanism and kinetics (**Figure 1**), OLC was synthesized at temperatures from 600-1800 °C. Raman spectroscopy characterized the OLC surface and XRD determined the size of the residual diamond core. Thermal analysis investigated the reactivity of the material, which saw a maximum at 900 °C, implying a less stable disordered carbon was formed as an intermediate step.[5] Using high temperature oxidation calorimetry, the standard enthalpies of formation at 25 °C of OLC with different structural ordering were investigated. In terms of enthalpy and depending on the degree of structural ordering, OLC can be up to

16 kJ mol^{-1} less stable than graphite but up to 27 kJ mol^{-1} more stable than their fullerene allotropes. Furthermore, OLC are approximately 5–9 kJ mol^{-1} less stable than single-wall carbon nanotubes. The samples prepared at 1800 °C are energetically less stable than samples made at 1300 and 1500 °C. These changes in energetics may stem from oxygen- containing functional groups bonded to the structure or from the creation of topological defects (polygonization and pentagon formation) whose concentration increases with increasing temperature and whose higher energy is balanced by configurational entropy.[6]

We coupled experimental characterization with computer modeling, specifically using a reactive force field that included long-range Coulomb and van der Waals interactions to analyze how a nanodiamond particle changes with time and temperature (**Figure 2**). The outer layers of the nanodiamond have a lower kinetic barrier to transformation, which is why they are converted to sp^2 carbon first. The nanodiamond inner core has a large size-dependent barrier that releases pressure and expands upon graphitization. A delicate balance between the thermal energy, long-range interactions, and the entropic/enthalpic free energy gained by graphitization thereby determines the degree of transformation at a particular temperature. The final structure is highly defective with many five- and seven-membered rings to curve space. Larger nanodiamonds with a diameter of 4 nm can graphitize into spiral structures with a large (29-atom carbon ring) pore opening on the outermost shell. Such a large one-way channel is most attractive for a controlled insertion of molecules/ions such as Li ions, water, or ionic liquids, for increased electrochemical capacitor or battery electrode.[7]

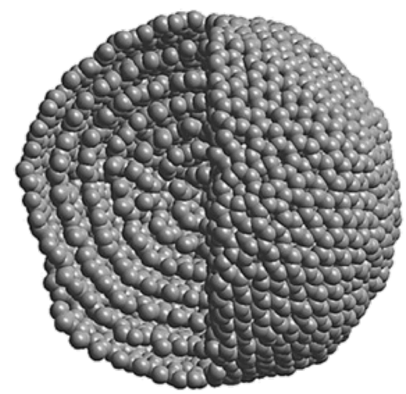

Figure 2. Computer simulation of a carbon onion made by annealing nanodiamond at 1800 °C.[7]

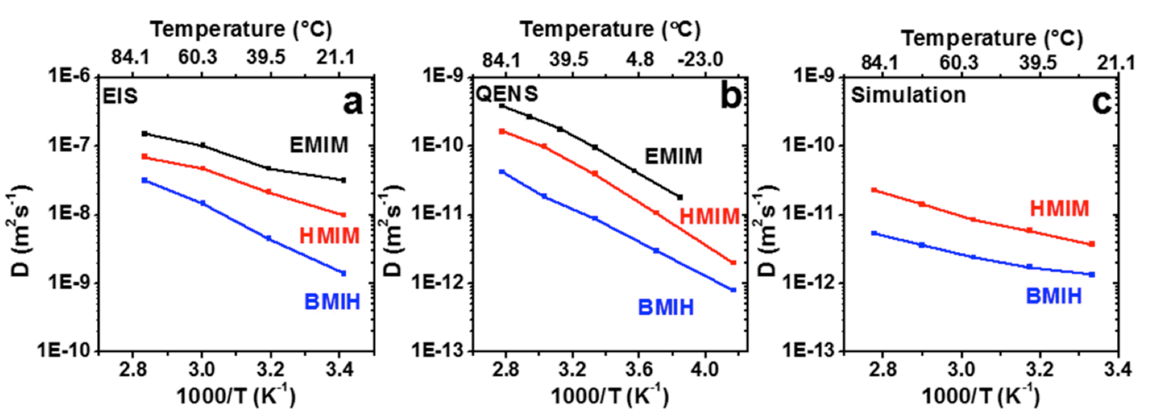

Figure 3. Diffusion constant as a function of temperature for three ionic liquids at the surface of OLC, calculated using three characterization techniques: electrochemical impedance spectroscopy, quasi-elastic neutron scattering, and molecular dynamics.[8]

Most recently, results from three areas of the FIRST Center combined our resources to analyze ionic liquids at the surface of OLC. Ionic liquids are gaining momentum in energy storage applications because of their unique properties such as wide voltage stability window, negligible vapor pressure, and wide temperature window. Electrochemical measurements from Drexel

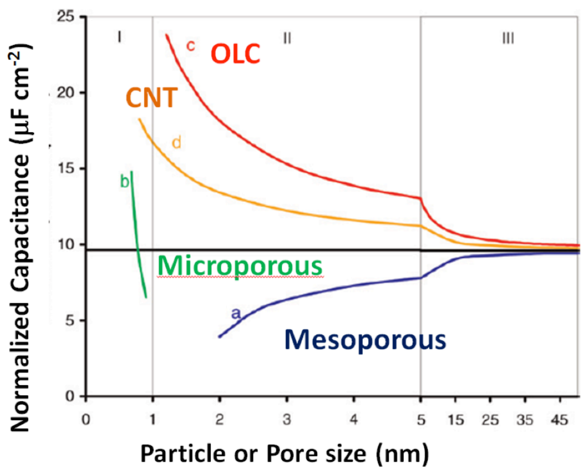

Figure 4. Normalized capacitances as a function of particle / pore size for carbons of various curvature.[4]

University, quasi-elastic neutron scattering from ORNL, and molecular dynamics from Vanderbilt University calculated diffusion coefficients (**Figure 3**) and found capacitance and resistance data that is vital to move the field forward.[8]

Significant Impacts on Science and Technology: Research on materials for EDLCs has traditionally focused on maximizing surface area by using highly porous materials. Our studies suggest that a very different material, one that has a closed surface with a smaller surface area, can outperform the porous materials. We also suggest that exohedral materials, such as OLCs, should be used to maximize the charge stored on the surface of a material (**Figure 4**).[4]

OLC is a carbon material that has many attractive properties, leading it to be a model system for fundamental studies. We have extensively investigated its structure and how ions behave in the double layer formed at the surface of the charged particle.

Publications and Manuscripts:

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