Final Report

Room-temperature Electrochemical Synthesis of Carbide-derived Carbons and Related Materials

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Abstract

This project addresses room-temperature electrochemical etching as an energy-efficient route to synthesis of 3D nanoporous carbon networks and layered 2D carbons and related structures, as well as provides fundamental understanding of structure and properties of materials produced by this method. Carbide-derived-carbons (CDCs) are a growing class of nanostructured carbon materials with properties that are desirable for many applications, such as electrical energy and gas storage. The structure of these functional materials is tunable by the choice of the starting carbide precursor, synthesis method, and process parameters. Moving from high-temperature synthesis of CDCs through vacuum decomposition above 1400°C and chlorination above 400°C, our studies under the previous DOE BES support led to identification of precursor materials and processing conditions for CDC synthesis at temperatures as low as 200°C, resulting in amorphous and highly reactive porous carbons. We also investigated synthesis of monolithic CDC films from carbide films at 250-1200°C. The results of our early studies provided new insights into CDC formation, led to development of materials for capacitive energy storage, and enabled fundamental understanding of the electrolyte ions confinement in nanoporous carbons.

In the project, we explored the possibility of room-temperature CDC synthesis and synthesis of carbon-sulfur nanolaminates. Moving away from gas chemistry, we studied electrochemical etching for removing metals from carbides. Avoiding complications related to using halogen gases, this approach introduces a safe room-temperature route to CDC synthesis, which has not been explored before. We conducted a systematic study of room-temperature formation and structure evolution of CDCs from binary and ternary carbides. Analytical tools such as electron microscopy, X-ray diffraction, X-ray photoelectron, Raman and infrared spectroscopies were employed to characterize the materials produced in this study. Pore volume and pore size distribution were studied by gas sorption. Mechanical properties were evaluated by nanoindentation, thermal analysis was used to study temperature stability of the materials, and extensive electrochemical characterization was performed. Binary carbides, such as SiC and TiC, and carbides in ternary systems Ti-Al-C (e.g., Ti_2AlC and Ti_3AlC_2), Ti-Si-C and Ti-S-C were studied. We conducted a comparative study of properties of carbides and determined which ones could be etched, as well as appropriate etchants and etching conditions. By developing a method for room-temperature conformal CDC formation, we were able to retain the morphology of the precursor carbide and produce functional films of porous carbons. Patterning of surface and localized synthesis enables direct manufacturing of devices (supercapacitors or sensors) on various substrates. Another advantage of the electrochemical etching of the metals from the carbide structure is that the etching processes can be controlled for selective removal of metal atoms from ternary carbide (e.g. MAX phase) structures. This resulted in a new and effective route for synthesis of layered nanostructures such as graphene-like carbon interleaved with sulfur layers, which showed promising properties for applications in lithium-sulfur batteries. The MAX phases form a large family of layered ternary carbides with the general formula $M_{n+1}AX_n$, where n = 1–3, M is an early transition metal, A is an A-group element (mostly IIIA and IVA), and X is C and/or N (e.g., Ti_2SC, Ti_3SiC_2). Selective electrochemical etching of metals from carbides in aqueous electrolytes allows synthesis of a variety of novel layered and two-dimensional (2D) materials. This work contributes to the development of a general selective extraction approach to novel materials produced from inorganic precursors.

Keywords: carbon, graphene, carbide selective extraction, synthesis, electrochemical properties

1 DOE Award # and name of the recipient (Institution)

DE-FG02-07ER46473, Drexel University
DE-FGOI-05ER05-01, Drexel University

2 Project title and name of the PI

Room-temperature Electrochemical Synthesis of Carbide-derived Carbons and Related Materials, Prof. Yury Gogotsi

Silicon Carbide Derived Carbons: Experiments and Modeling, Prof. Yury Gogotsi (Collaborative grant with Miklos Kertesz, Georgetown University)

3 Date of the report and period covered by the report

September 1, 2007 – February 28, 2015

4 A brief description of accomplishments

4.1 <u>Room-temperature synthesis of CDC by electrochemical etching of SiC</u>

The formation of a carbide-derived carbon (CDC) layer on silicon carbide ceramics (SiC) was achieved by electrochemical etching in a nonaqueous electrolyte at room temperature. The selective etching of Si from SiC in a single step reaction at steady state conditions using HF in different organic solvents was carried out and the role of polarity, surface tension, density, and viscosity of the organic solvents in the formation of the carbon layer has been investigated.

Solution of HF in ethanol allows the best control over selective etching of Si forming amorphous and graphitic carbon on the SiC surface at 10 and 20 mA/cm^2, respectively. At an optimum current density, HF solution in ethanol minimizes the activity of OH ion and inhibits the formation Si-OH intermediate, preventing the formation of SiO_2. The presence of an intense G band of graphitic carbon in Raman spectra and high resolution transmission electron microscopy analysis clearly indicate formation of graphitic carbon on the surface of SiC (Figure 1). X-ray diffraction shows that the etching rate of α-SiC is much higher when compared to β-SiC at steady state condition.

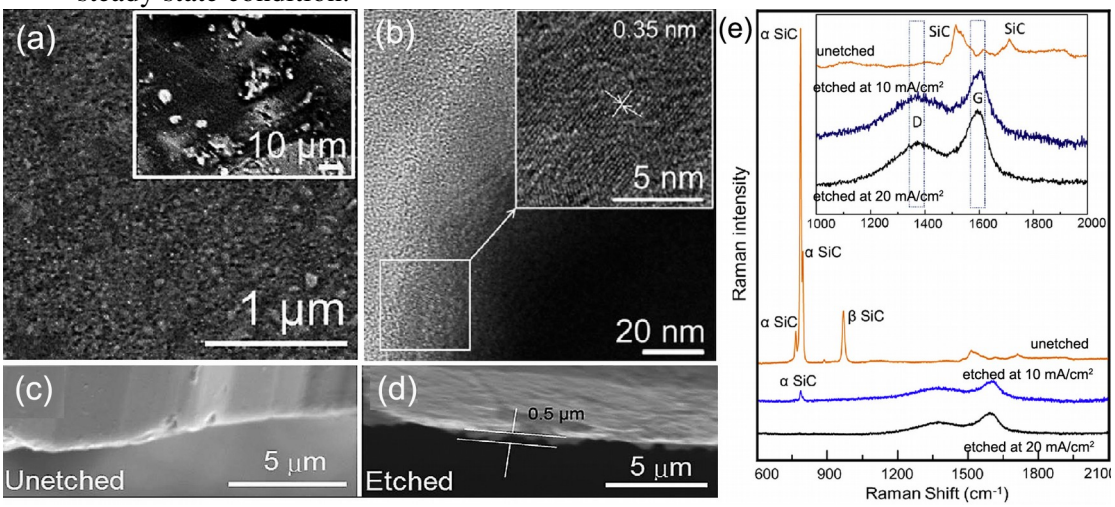


Figure 1. (a) SEM and (b) TEM images of SiC etched in HF solution in ethanol at 20 mA/cm^2; Cross-sectional SEM images of the SiC (c) before and (d) after etching in HF solution in ethanol at 20 mA/cm^2; (e) Raman spectra of the SiC before and after etching.

4.2 Room-Temperature CDC Synthesis by Electrochemical Etching of MAX Phases

Room-temperature synthesis of CDC was achieved by electrochemically selectively extract the metal atoms from ternary layered carbides, Ti_3AlC_2, Ti_2AlC and Ti_3SiC_2 (MAX phases). The result was a predominantly amorphous carbide derived carbon, with a narrow distribution of micropores. The latter was produced by placing the carbides in HF, HCl or NaCl aqueous solutions and applying anodic potentials. The pores that form when Ti_3AlC_2 was etched in dilute HF are ~ 0.5 nm in diameter. The kinetics were linear and thus the process must be controlled by the interfacial reaction and was highly scalable.This approach forgoes energy-intensive thermal treatments and presents a novel method for developing carbons with finely tuned pores for a variety of applications, such as supercapacitor and battery electrodes or CO_2 capture.

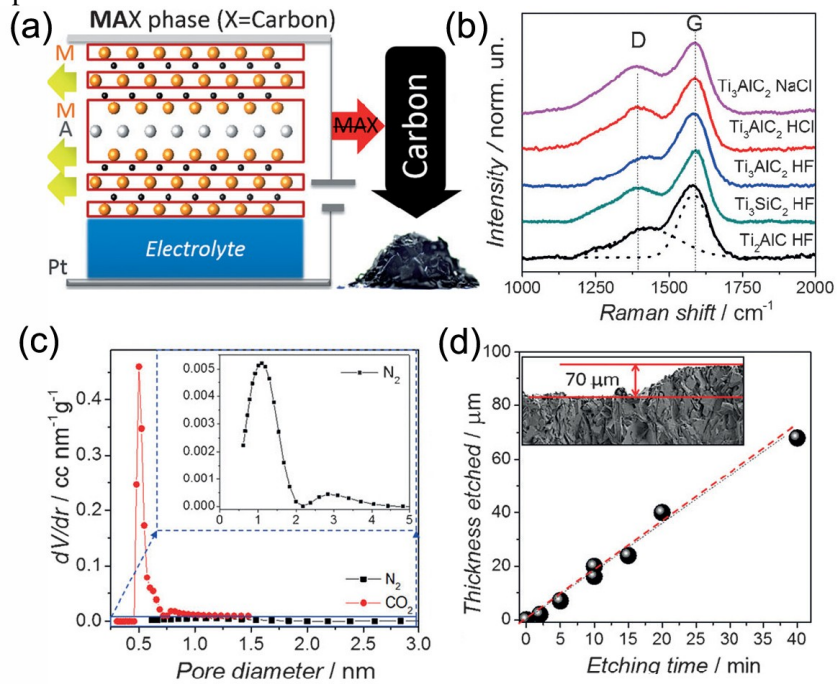


Figure 2. (a) Schematic representation of the room-temperature CDC synthesis from MAX phase; (b) Raman spectra of select carbon synthesized from Ti_3SiC_2, Ti_3AlC_2, and Ti_2AlC in HF and Ti_3AlC_2 in HCl and NaCl electrolytes. (c) Pore size distribution for the Ti_3AlC_2 CDC obtained by CO_2 and N_2 gas sorption (inset). (d) Time-dependence of etched thickness for Ti_3AlC_2 sample etched in 5 wt.% HF at a constant current of 100 mA/cm^2. Inset: SEM image of the etching profile.

4.3 Study on ionic transport in CDC films

The formation of carbon/sulfur (C/S) nanolaminates at room temperature was achieved by electrochemically and selectively extracting Ti from the MAX phase Ti_2SC. The products were composed of multi-layers of C/S flakes, with predominantly amorphous and some graphene-like structures. Covalent bonding between C and S is observed in the nanolaminates, which render the latter promising

candidates as electrode materials for Li-S batteries. It was also shown that it was possible to extract Ti from other MAX phases, such as Ti_3AlC_2, Ti_3SnC_2, and Ti_2GeC, suggesting that electrochemical etching can be a powerful method to selectively extract the "M" elements from the MAX phases, to produce "AX" layered structures, that cannot be made otherwise.

Considering that >70 MAX phases are known to exist, it is not difficult to foresee that the "AX" structures represent a large new family of nanostructured materials, much of which will probably be 2D. The various "A" and "X" combinations known render the "AX" structures highly attractive for a number of potential applications, such as electrical energy storage, catalysis, etc. Synthesis of these new "AX" structures, as well as, their structural and property characterization certainly represent a very fertile area of research, with potentially huge payoffs.

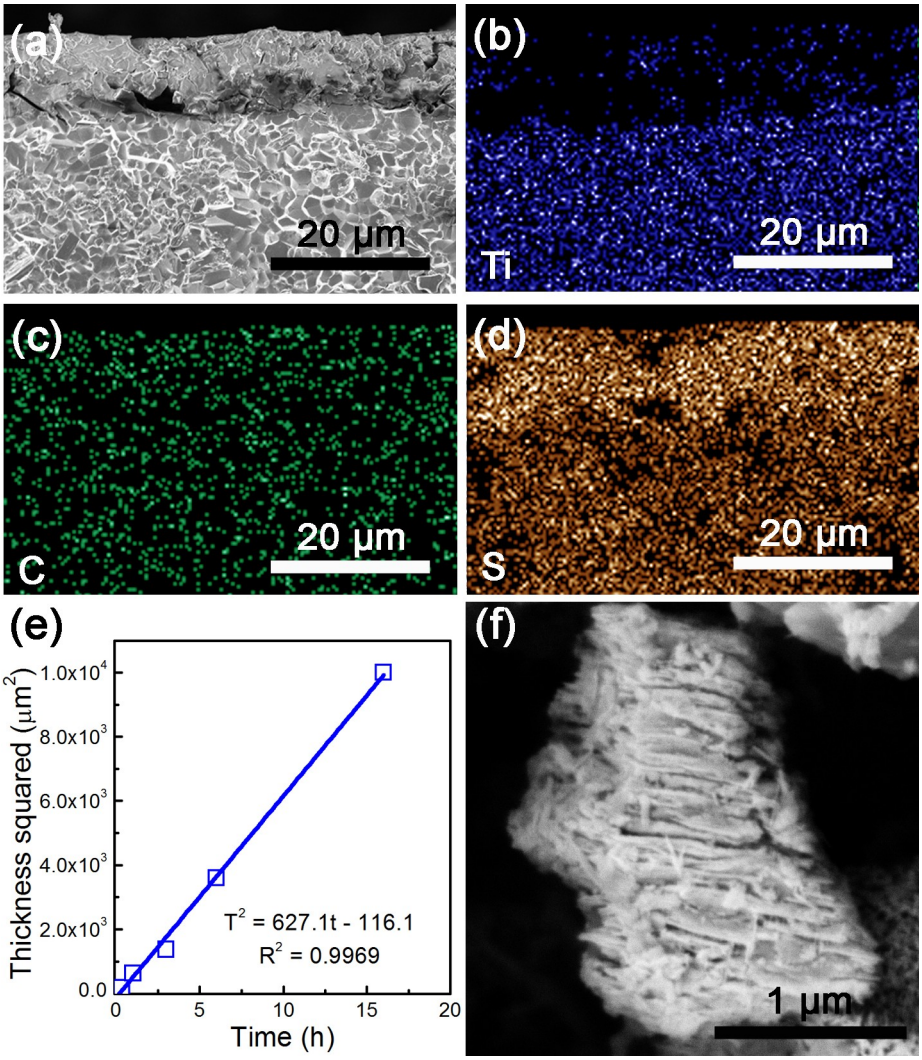


Figure 3. (a) Cross-sectional SEM image of a Ti_2SC sample etched for 1 h at 0.6 V in 0.5 M NH_4F aqueous solution and (b–d) corresponding EDS maps, indicating the selective extraction of Ti; (e) C/S layer thickness vs. etching time at 0.8 V; (f) SEM image of an as-synthesized C/S particle.

5 List of papers (already published) in which DOE support from Grant # DE-FG02-07ER46473 (ER46473) is acknowledged.

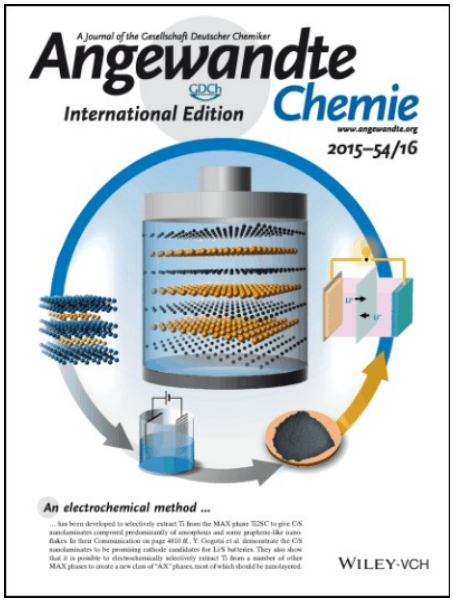
Papers originating from the latest grant period (September 1, 2013 – February 28, 2015)

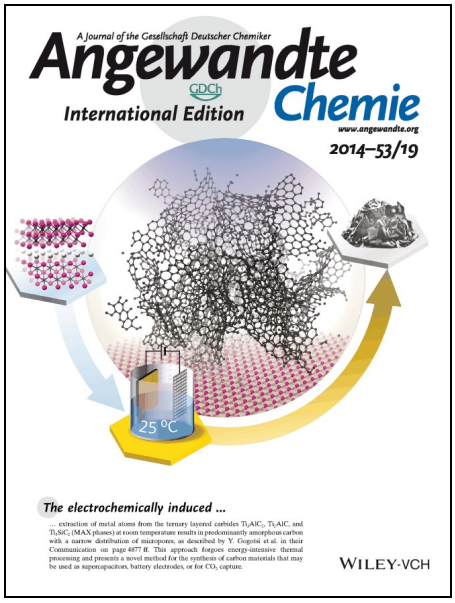
1. G. Cambaz-Buke, G. Yushin, V. Mochalin, Y. Gogotsi, Effect of Defects on Graphitization of SiC, *J. Mater Res.* **28** (7) 952-957 (2013)
2. P. Huang, M. Heon, D. Pech, M. Brunet, P.-L. Taberna, Y. Gogotsi, S. Lofland, J. D. Hettinger, P. Simon, Micro-supercapacitors from Carbide Derived Carbon (CDC) Films on Silicon Chips, *J. Power Sources* **225**, 240-244 (2013) **(ISI Highly Cited Paper)**
3. A. C. Forse, J. M. Griffin, H. Wang, N. M. Trease, V. Presser, Y. Gogotsi, P. Simon, C. P. Grey, Nuclear Magnetic Resonance Study of Adsorption of Electrolyte Ions on Carbide-derived Carbon, *Phys. Chem. Chem. Phys*., **15**, 7722-7730 (2013)
4. C. R. Pérez, S.-H. Yeon, J. Ségalini, V. Presser, P.-L. Taberna, P. Simon, Y. Gogotsi, Structure and Electrochemical Performance of Carbide-Derived Carbon Nanopowders, *Advanced Functional Materials* **23**, 1081–1089 (2013) **(ISI Highly Cited Paper)**
5. M. R. Lukatskaya, J. Halim, B. Dyatkin, M. Naguib, Y. S. Buranova, M. W. Barsoum, Y. Gogotsi, Room-temperature carbide derived carbon synthesis by electrochemical etching of MAX phases, *Angewandte Chemie Int. Edition*, **53** (19) 4877-4880 (2014) **(cover article)**
6. J. Senthilnathan, C.C. Weng, W.T. Tsai, Y. Gogotsi, M. Yoshimura, Synthesis of carbon films by electrochemical etching of SiC with hydrofluoric acid in nonaqueous solvents, *Carbon*, **71**, 181-189 (2014)
7. A. C. Forse, J. M. Griffin, V. Presser, Y. Gogotsi, C. P. Grey Ring Current Effects: Factors Affecting the NMR Chemical Shift of Molecules Adsorbed on Porous Carbons, *J. Phys. Chem. C,* **118** (14) 7251-7740 (2014)
8. Y. Gogotsi, Not Just Graphene - the Wonderful World of Carbon and Related Nanomaterials, *MRS Bulletin*, **40**, 1110-1120 (2015) (**Fred Kavli Lecture**)
9. M.-Q. Zhao, M. Sedran, Z. Ling, M.R. Lukatskaya, O. Mashtalir, M. Ghidiu, B. Dyatkin, D. J. Tallman, T. Djenizian, M. W. Barsoum, Y. Gogotsi, Synthesis of Carbon/Sulfur Nanolaminates by Electrochemical Extraction of Titanium from Ti_2SC, *Angewandte Chemie, Int. Edition*, **54** (16) 4810–4814 (2015) (**cover article**)

Earlier papers acknowledging this grant **# DE-FGOI-05ER05-01**
(September 1, 2007 – August 31, 2013)

10. I. Laszlo, M. Kertesz, Y. Gogotsi, Simulations of Multi-atom Vacancies in Diamond, In Multiscale Modeling of Materials, Ed. by R. Devanathan, M. J. Caturla, A. Kubota, A. Chartier, S. Phillpot (*Mater. Res. Soc. Symp. Proc. 978E*, Warrendale, PA, (**2007**), GG13-15.
11. T. Kyotani, J. Chmiola, Y. Gogotsi, Carbide Derived Carbon and Templated Carbons, in *Carbons and composites for electrochemical energy storage systems*, edited by F. Beguin and E. Frackowiak, CRC Press/Taylor and Francis, (2008). In press
12. Y. Gogotsi, P. Simon, Foreword, in *Nanostructured Materials in Electrochemistry*, edited by A. Eftekhari, WILEY-VCH, Weinheim, Germany, pp. XVII-XIX (2008).

13. C. Portet, J. Chmiola, Y. Gogotsi, S. Park, K. Lian, Electrochemical Characterizations of Carbon Nanomaterials by the Cavity Microelectrode Technique, *Electrochimica Acta*, *53*(26), 7675-7680 (2008).
14. C. Portet, G. Yushin, Y. Gogotsi, Effect of carbon particle size on electrochemical performance of supercapacitors, *J. Electrochemical Society 155*(7), A531-A536 (2008).
15. Z. G. Cambaz, G. Yushin, S. Osswald, V. Mochalin, Y. Gogotsi, Noncatalytic Synthesis of Carbon Nanotubes, Graphene and Graphite on SiC, *Carbon* **46** (6) 841-849 (2008)
16. C. Largeot, C. Portet, J. Chmiola, P.L. Taberna, Y. Gogotsi, P. Simon, Relation between the Ion Size and Pore Size for an Electric Double-Layer Capacitor, *J. Am. Chem. Soc*. **130** (9), 2730-2731 (2008)
17. P. Simon, Y. Gogotsi, Materials for Electrochemical Capacitors, *Nature Materials* **7**(11) 845-854 (2008)
18. J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, Desolvation of ions in subnanometer pores, its effect on capacitance and double-layer theory, *Angewandte Chemie Int. Edition* **47** (18), 3392-3395 (2008)
19. C. Portet, M. Á. Lillo-Ródenas, A. Linares-Solano, Y. Gogotsi, Capacitance of KOH activated carbide-derived carbons, *Phys. Chem. Chem. Phys*. **2009**, in press
20. S. Pathak, Z. G. Cambaz, S. R. Kalidindi, J. G. Swadener, Y. Gogotsi, Viscoelasticity and high buckling stress of dense carbon nanotube brushes *Carbon*, **2009**, 47, 1969-1976.
21. T. Kyotani, J. Chmiola, Y. Gogotsi, Carbide Derived Carbon and Templated Carbons, Chapter 3 in *Carbon Materials for Electrochemical Energy Storage Systems*, edited by F. Beguin and E. Frackowiak, CRC Press/Taylor and Francis, pp. 77-113 (2009).
22. R. Lin, P.L. Taberna, J. Chmiola, D. Guay, Y. Gogotsi, P. Simon, Microelectrode study of pore size, ion size and solvent effects on the charge/discharge behavior of microporous carbons for electrical double layer capacitors, *Journal of the Electrochemical Soc.* **156** (1) A7-A12 (2009)
23. C. Portet, D. Kazachkin, S. Osswald, Y. Gogotsi, E. Borguet, Impact of Synthesis Conditions on Surface Chemistry and Structure of Carbide-Derived Carbons, *Thermochimica Acta*, *497*(1), 137-142 (2010).
24. J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, Monolithic Carbide-Derived Carbon Films for Micro-Supercapacitors, *Science*, **328**, 480-483 (2010) **(ISI Highly Cited Paper)**
25. V. Presser, J. McDonough, S.-H. Yeon, Y. Gogotsi, Effect of Pore Size on Carbon Dioxide Sorption by Carbide Derived Carbon, *Energy & Environmental Science*, **4** (8), 3059 - 3066 (2011) **(ISI Highly Cited Paper)**
26. V. Presser, L. Zhang, J. J. Niu, J. McDonough, H. Fong, Y. Gogotsi, Flexible Nano-Felts of Carbide-Derived Carbon with Ultra-High Power Handling Capability, *Advanced Energy Materials*, **1**, 423–430 (2011) **(Cover article)**
27. V. Presser, M. Heon, Y. Gogotsi, Carbide-Derived Carbons - From Porous Networks to Nanotubes and Graphene, *Advanced Functional Materials*, 21 (5) 810-833 (2011) **(Feature and Cover article; ISI Highly Cited Paper)**
28. M. Heon, S. Lofland, J. Applegate, R. Nolte, E. Cortes, J. D. Hettinger, P.-L. Taberna, P. Simon, P. Huang, M. Brunet, Y. Gogotsi, Continuous Carbide-Derived Carbon Films with High Volumetric Capacitance, *Energy & Environmental Science* 4, 135-138 (2011)
29. S. Osswald, J. Chmiola, Y. Gogotsi, Structural Evolution of Carbide-Derived Carbons upon Vacuum Annealing, *Carbon*, **50** (13) 4880-4886 (2012)





6 A list of people working on the project – graduate students, postdocs, visitors, technicians, etc. Indicate for each whether receiving full or partial support. In case of partial support indicate percentage of support.

- Prof. Yury Gogotsi (PI; partial, 8.33%)
- Dr. Ranjan Dash, post-doctoral associate, 58.33%
- Mr. Min Heon, PhD student, 100%, graduated with PhD degree
- Carlos Perez – PhD student, NSF IGERT Fellow, 41.66%, graduated with PhD degree
- Daniel Vryhof, undergraduate student (senior design project, no DOE support)
- Dr. Meng-Qiang Zhao, currently post-doc at the University of Pennsylvania
- Min Heon (graduate student; 100%) graduated with PhD degree
- Maria Lukatskaya (graduate student; 41.66%) graduated with PhD degree
- John McDonough (graduate student; 25%) graduated with PhD degree
- Michael Abdelmalak, graduate student 25%, graduated with PhD degree
- Boota Muhammad, graduate student 100%
- Katherine Van Aken, graduate student 66.66%
- Juliette Billard, exchange student 25%
- Bastian Etzold, post-doctoral associate 41.66%
- Sun-Hwa Yeon, postdoctoral associate 25%
- Vadym Mochlain, postdoctoral associate 33.33%
- Muge Acik, postdoctoral associate 58.33%
- Majid Beidaghi, postdoctoral associate 16.66%

7 An updated list of other support (current and pending, federal and non-federal). For each, indicate the overlap, if any, and/or distinctiveness with the DOE-supported project. This can be brief (one or two sentences).

- **Energy Frontier Research Center** (EFRC-FIRST, Agency: DoE). This interdisciplinary energy center is using micro- and mesoporous carbon, graphene, and carbon onions provided by Drexel to improve the understanding of the processes and properties at the fluid solid interface (FSI). Complements the current project. While the current project focuses on low-temperature synthesis of carbide-derived carbon from binary and ternary carbides, the EFRC efforts are directed towards carbon onions, high-temperature CDC, nanodiamond and graphene. Submicrometer films and nanopowders used to enable CDC synthesis at low temperatures and to understand the unique structure of carbon produced under those conditions are not covered by the EFRC effort.
- **International Collaboration in Chemistry: Ionic Liquid in Confined Environments** (Agency: NSF). In collaboration with Prof. Kornyshev (Imperial College, London) the behavior of ionic liquids (ILs) confined in nanoporous carbon is studied and correlated with experimental data.
- **New Materials Synthesis and Processes for Energy Storage Microdevices** (Agency: PUF of the French Embassy). Research is directed at improved performance of CDC / carbon onion devices. This is a small grant supporting travel and short-term student exchange.
- **Development of Electrode Architectures for High Energy Density Electrochemical Capacitors** (Agency: Sandia National Laboratories) This project is geared toward the development of large-scale pseudo-capacitive energy storage devices based on low-cost carbons with mesoporosity.
- **New Layered Nanolaminates for Use in Lithium Battery Anodes** (Agency: DoE, BATT Program) This project focuses on the development of laminate MAX-phase based anode materials that combine the laminate structure of graphite with silicon, tin and other elements that can provide a higher Li uptake per atom and lead to an improved capacity, lesser expansion, longer cycle life and a lower cost compared to current Li-ion battery anodes.

8 Unexpended funds: Indicate the amount of unexpended funds, if any that are anticipated to be left at the end of the current budget period. If the amount exceeds 10 percent of the funds available for the current budget year, provide information as to why the excess funds are anticipated to be available and how they will be used in the next budget.

None