Development of Electrode Architectures for High Energy Density Electrochemical Capacitors

Majid Beidaghi[1], Maria Lukatskaya[1], Emilie Perre[2], Ryan P. Maloney[2], Yury Gogotsi[1], Bruce Dunn[2]

[1] Department of Materials Science and Engineering and A.J. Drexel Nanotechnology Institute, Drexel University, USA

[2]Department of Materials Science and Engineering, University of California – Los Angeles, Los Angeles, CA, USA

Introduction

The principal goal of the present research is to create an electrode architecture for electrochemical capacitors (ECs) that possesses both the high specific power of carbon supercapacitors and the high specific energy of pseudocapacitive materials. The design and fabrication of these electrodes are based on the nanoscale deposition of transition metal oxides onto mesoporous carbon-based supports. Extraction of metals from carbides can generate a broad range of carbon nanostructures, which are known as Carbide-Derived Carbons (CDCs). The structures of CDCs as well as their pore size distribution depend on the crystal structure of the carbide precursor as well as process parameters including temperature, time and environment. Nanoscale transition metal oxides such as niobium oxide (Nb_2O_5) can be easily synthesized on the CDC surface via an aqueous hydrothermal route. The oxide size can be tailored to match the CDC porosity, allowing for optimization of ionic and electronic transport within the electrode. A key feature with these architectures is that each component possesses interconnected mesoporosity to facilitate electrolyte access to both phases.

Experimental

Carbide Powder — Begin with a carbide precursor, such as SiCN, Ti_3SiC_2, or $TiAlC_2$

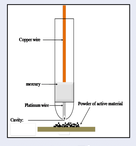
Cl_2 200-1200°C — Remove metals via chlorination

H_2 200-600°C — Anneal structure in flowing hydrogen

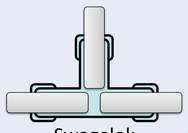
Carbide Derived Carbon (CDC) — Resulting Carbide Derived Carbon with tailored morphology

Hydro-thermal Synthesis 200°C 96 hours ← Deposit metal-oxide onto CDC
- Ammonium niobate oxalate hydrate
- Phenylphsophonic acid
- Urea

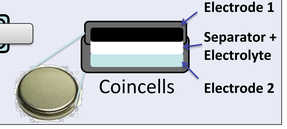
Nb_2O_5-CDC Composite — Resulting Carbide Derived Carbon with metal-oxide nanoparticles for increased specific energy



Microcavity Electrodes



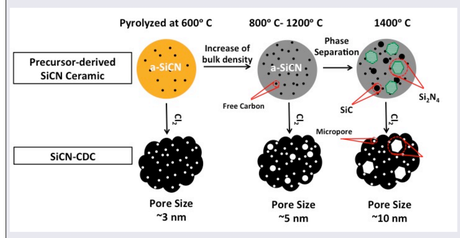
Swagelok cells

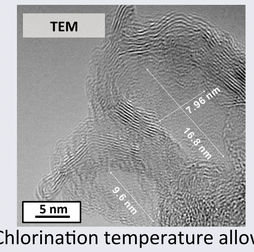


Coincells

Results

SiCN-CDC

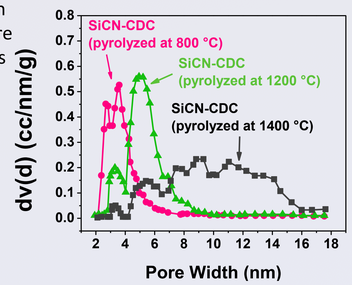




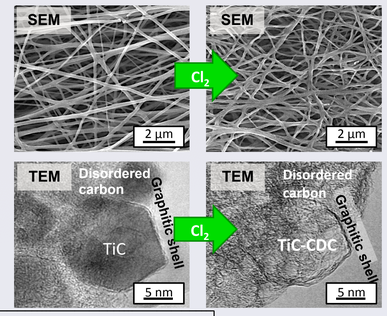
Chlorination temperature allows tailoring of carbon mesoporosity while maintaining macrostructure

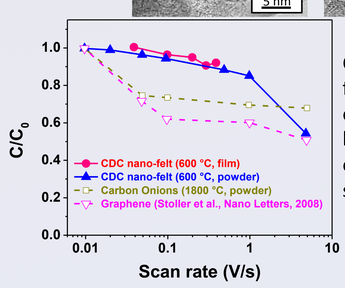
Carbide Derived Carbon (CDC) has a high surface area due to small pores. The pore size is tailorable, from a few nanometers up to tens of nanometers wide, by controlling pyrolisis temperature.

Increasing the pyrolysis temperature increased the amount of mesopores in the resulting CDC.



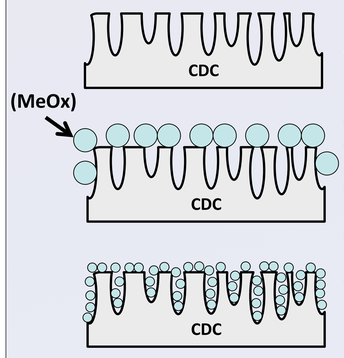
TiC-Nanofelt CDC





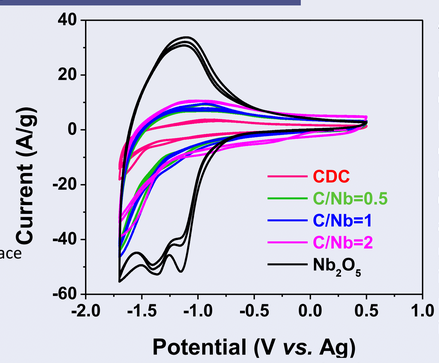
CDC nanofelts tested as fiber-electrodes outperform the power handling ability of carbon onions at intermediate scan rates (up to 2 V/s)

Nb_2O_5-CDC Composite



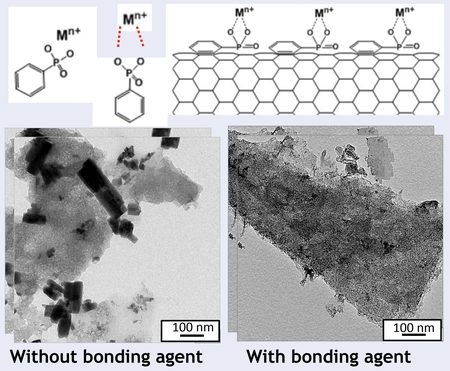
The size of the oxide particles must be tailored to match the pore size of the CDC. Too large particles will occlude the pores, preventing utilization of the CDC's high surface area.

Oxide particles tuned to fit within the small pores make effective use of the high surface area of the CDC



At a scan rate of 50 mV/s, with 1M $LiClO_4$ in acetonitrile electrolyte, the Nb_2O_5-CDC composites (with various C:Nb ratios) display increased capacities compared with the CDC alone.
Other aqueous and non-aqueous electrolytes proved undesirable, either due to instability of the solvent at the required potentials or lower ionic conductivities.

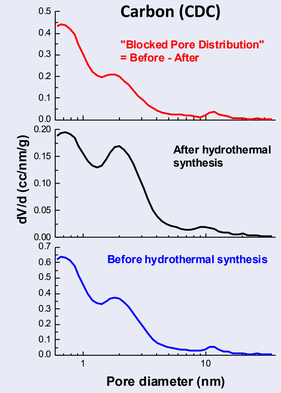
Phenylphosphonic Acid bonding agent drastically reduces metal-oxide particle size



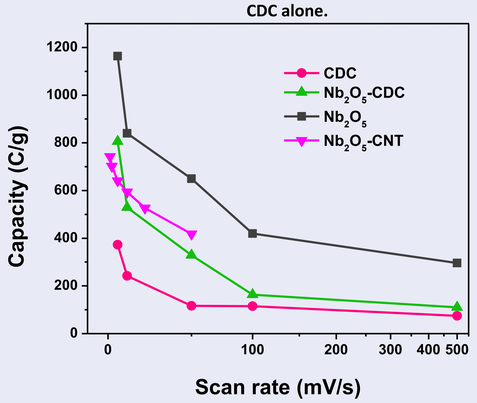
Without bonding agent - 100's nm

With bonding agent -10's nm

Smaller particles fill micro- and mesoporosity of Carbide-Derived Carbon (CDC)



The Nb_2O_5-CDC composite electrodes demonstrate higher capacities at different scan rates compared to CDC alone.



Conclusions

- CDC with hierarchical pore structure (micropores & mesopores with mean pore size, 3–10 nm) and large BET surface area, up to 2400 $m^2\ g^{-1}$, were synthesized by etching amorphous or crystalline polymer-derived SiCN ceramics.
- Micropores form by etching Si atoms from the SiC phase, while mesopores derive from the elimination of Si–N moieties. The resulting morphology (pore size, PSD, and SSA) strongly depends on pyrolysis temperature of the preceramic polymer, as well as on etching conditions.
- Mechanically flexible TiC-CDC nano-felts were developed through chlorination of electrospun TiC nano-fibrous felts. The TiC-CDC nano-felts retained the morphological properties of the precursor, while had substantially higher values of SSA and pore volume.
- Nanoscale Nb_2O_5 can be easily synthesized within the pores of CDC support.
- Capacitance measurements for the Nb_2O_5-CDC material shows a high level of energy storage, significantly higher than CDC.

Future Work

- Scale up production of Nb_2O_5-CDC composite powder
- Incorporate powder into coin cell devices
- Optimize coin cell electrode loading and morphology for enhanced specific energy and power

Acknowledgements

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