Nanostructured tunable mesoporous carbon for energy and biomedical applications

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Abstract

We will discuss synthesis of carbide-derived carbon (CDC), which is a nanoporous carbon formed by selectively etching metal atoms from metal carbides [1]. CDCs are generally produced by chlorination of carbides in the 200–1200°C temperature range. Metals and metalloids are removed as chlorides, leaving behind a noncrystalline carbon with up to 80% open pore volume. A wide range of carbide precursors (TiC, SiC, B4C, VC, Mo2C, NbC as well as ternary carbides – Ti3AlC2, Ti2AlC, also known as MAX-phases) leads to a wide range of carbons with tailored porosity. The total volume and characteristic dimensions of meso- and nanopores can be predicted and achieved by selection of a binary or ternary carbide and variation of the chlorination process parameters. Due to a wide range of pore sizes (0.3–30 nm) and specific surface areas (300–2300 m2/g) of CDCs, a great potential for applications requiring large volumes of either micropores.

The highly tunable porosity of CDC [1,2] has inspired fundamental studies of the effects of pore size, pore volume, and surface area on transport and adsorption of gases, ions and biomolecules. The unique properties of CDC allowed to use it in many demanding applications including H2 and methane storage, gas sorption, adsorbents, electrodes in batteries and supercapacitors [3], flow capacitors, molecular sieves, catalyst supports, water/air filters and medical devices, protein adsorption, tribology, extracorporeal devices for blood cleansing [4]. Such properties of CDC as good electrical conductivity combined with high surface area, large micropore volume, and pore size control allow its application as active material in electrodes for flow desalination [5], supercapacitors [6] as porous electrodes for capacitive deionization [7].

Chlorination of layered ternary MAX-phase carbides has made it possible to synthesize mesoporous carbons with large volumes of slit-shaped mesopores that can be used for purification of bio-fluids due to their excellent biocompatibility and ability to adsorb a range of inflammatory cytokines within the shortest time, which is crucial in sepsis treatment. The synthesized carbons, having tunable pore size with a large volume of slit-shaped mesopores, outperformed other materials in terms of efficiency of TNF-α removal. Cytokine removal from blood may help to bring under control the unregulated pro- and anti-inflammatory processes driving sepsis. Adsorption can remove toxins without introducing other substances into the blood. Therefore, hemoadsorption might have advantages over hemofiltration, having the same or better efficiency in the treatment of inflammatory diseases, being of lower cost and offering considerably better comfort for patients during and after the treatments [8].

Large mesopores in CDC from MAX phases are capable to accommodate most of the proteins due to their controlled porosity can be used for separation of different proteins molecules.

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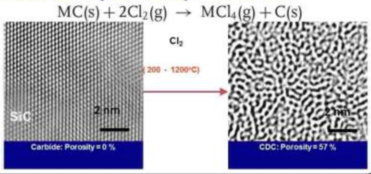
Carbide-Derived Carbons (CDCs) Process

- Cl_2 etching of metal carbides: TiC, SiC, Ti_3AlC_2, Mo_2C, Ti2AlC, Ti3AlC2, etc.
- Highly tunable pore structure
- Specific surface area 900 – 2100 m²/g

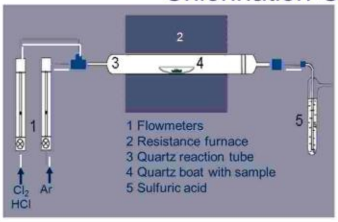
Methods of pore size control
- Precursors choice
- Synthesis conditions

Metals and metalloids are removed as chlorides, leaving behind a collapsed noncrystalline carbon with open pore volume

$$MC(s) + 2Cl_2(g) \rightarrow MCl_4(g) + C(s)$$



Chlorination Set-up



T=200-1200° C,

Ambient Pressure

Total volume and characteristic dimensions of meso- and nanopores can be predicted and achieved by selection of a binary or ternary carbide and variation of the chlorination process parameters.

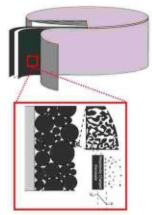
Large-scale production alternatives:
Fluidized-bed furnace or rotary kiln reactor

Applications of CDCs

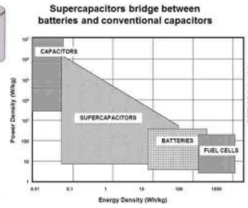
The highly tunable porosity of CDC has inspired fundamental studies of the effects of pore size, pore volume, and surface area on transport and adsorption of gases, ions and biomolecules. The unique properties of CDC allowed to use it in many demanding applications:

- H2 and Methane storage
- gas sorption
- absorbents
- electrodes in batteries and supercapacitors, flow capacitors
- capacitive desalination and deionization
- catalyst supports
- molecular sieves
- water/air filters and medical devices
- protein adsorption
- tribology
- extracorporeal devices for sepsis treatment

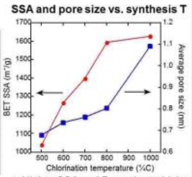
CDC for Supercapacitors



Supercapacitors bridge between batteries and conventional capacitors



SSA and pore size vs. synthesis T



Store charge electrostatically as charged ions "adsorbed" to oppositely charged surfaces

No charge transfer reactions take place, eliminating many shortcomings of traditional batteries

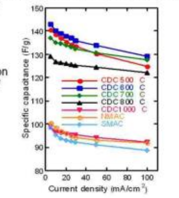
High specific surface area that is accessible to the electrolyte is crucial - porosity control is a requisite for high performance

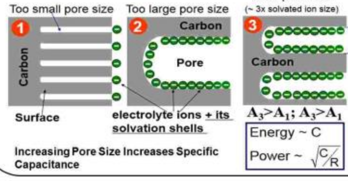
ELECTRODE OPTIMIZATION CRUCIAL FOR MAXIMIZING PERFORMANCE

Supercapacitors are able to attain greater energy densities while still maintaining the high power density of conventional capacitors.

Supercapacitors are a potentially versatile solution to a variety of emerging energy applications based on their ability to achieve a wide range of energy and power density.

- Higher SSA and Pore size at higher temperature
- Specific capacitance should **increase** with synthesis temperature



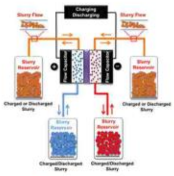


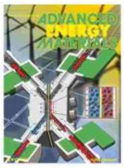
Increasing Pore Size Increases Specific Capacitance

- *Decreasing* pore size allowed a 50% increase in specific capacitance above the most advanced activated carbons commercially available
- The decrease in capacitance for small pore samples at high current densities is negligible - ion transport in small pores is still fast

CDC for Flow Capacitor Electrodes and Capacitive Deionization

The electrochemical flow capacitor uses a flow cell architecture, similar to existing redox flow batteries for grid storage, consisting of an electrochemical cell connected to external electrolyte reservoirs.



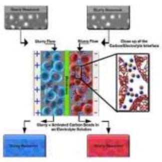


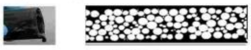
However, this technology is unique in that it uses a flowable slurry of capacitive particles suspended in a liquid electrolyte carrier fluid.

Uncharged slurry is pumped through a flow cell, where energy is stored capacitively within the solid particles. The charged slurry can then be held in reservoirs until the energy is needed, at which time the entire process is reversed.

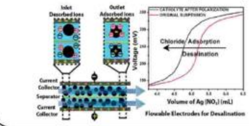
Schematic of the operation of an EFC system

Slurries are charged in the flow cell and stored in separate containers. They are pumped back to the cell for discharge.





New type of capacitive deionization (CDI) system

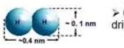


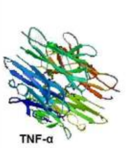
This capacitive deionization (CDI) system is based on capacitive suspension electrodes (CSEs). It was developed for desalting brackish and sea water through the use of flowable carbon suspensions.

Capacitive suspension electrodes can be envisioned to desalt water without the aid of ion exchange membranes

CDC for Protein Adsorption

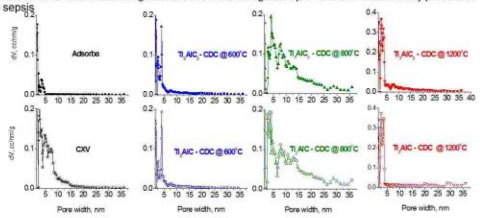
Hydrogen





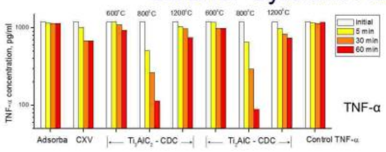
TNF-α
9.4 x 9.4 x 11.7 nm

- Severe sepsis kills 1,500 people/day (comparable to lung and breast cancer (~ 2,700 and ~ 1,100 people /day, respectively)
- Inflammatory response is driven by a complex network of cytokines, inflammatory mediators
- Cytokine removal from blood brings under control the unregulated pro- and anti-inflammatory processes driving sepsis



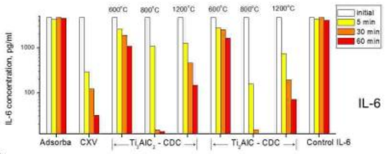
PSD in the 1.5 - 36 nm range obtained from N_2 sorption isotherms: commercial carbons and CDC from MAX phase ternary carbides

CDC for Cytokine Adsorption



TNF-α

Cytokines are regulatory proteins that are released by cells of the immune system and need to be removed from the blood in case of an autoimmune disease

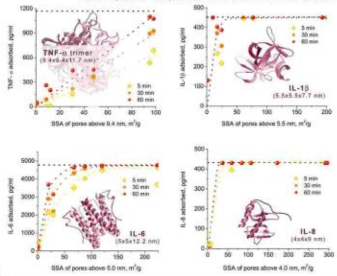


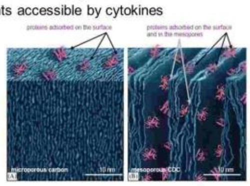
IL-6

CDC outperformed commercial carbons in the efficiency of cytokine's removal

CDC for Cytokine Adsorption

Adsorption depends on the SSA of adsorbents accessible by cytokines





Schematics of protein adsorption by porous carbons:

(A) Surface adsorption in microporous carbon. Small pores do not allow to be adsorbed in the bulk of carbon particles

(B) **(B)** Adsorption in the bulk of mesoroporous CDC. Large mesopores are capable to accommodate most of the proteins.

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