



# High capacitance of coarse-grained carbide derived carbon electrodes



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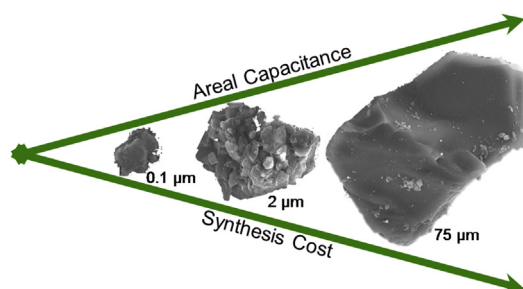
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## HIGHLIGHTS

- High capacitance and power density of coarse-grained porous carbon supercapacitors.
- Lower synthesis and manufacturing costs.
- Greater mass loading for grid and automotive electrical energy storage.
- Superior performance than activated carbon in different electrolytes.
- Expanded operating voltage window.

## GRAPHICAL ABSTRACT



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## ABSTRACT

We report exceptional electrochemical properties of supercapacitor electrodes composed of large, granular carbide-derived carbon (CDC) particles. Using a titanium carbide (TiC) precursor, we synthesized 70–250 μm sized particles with high surface area and a narrow pore size distribution. Electrochemical cycling of these coarse-grained powders defied conventional wisdom that a small particle size is strictly required for supercapacitor electrodes and allowed high charge storage densities, rapid transport, and good rate handling ability. The material showcased capacitance above 100 F g<sup>-1</sup> at sweep rates as high as 250 mV s<sup>-1</sup> in organic electrolyte. 250–1000 micron thick dense CDC films with up to 80 mg cm<sup>-2</sup> loading showed superior areal capacitances. The material significantly outperformed its activated carbon counterpart in organic electrolytes and ionic liquids. Furthermore, large internal/external surface ratio of coarse-grained carbons allowed the resulting electrodes to maintain high electrochemical stability up to 3.1 V in ionic liquid electrolyte. In addition to presenting novel insights into the electrosorption process, these coarse-grained carbons offer a pathway to low-cost, high-performance implementation of supercapacitors in automotive and grid-storage applications.

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## 1. Introduction

Electrochemical capacitors (also known as supercapacitors or

ultracapacitors), which rely on the electrosorption of ions by porous carbon electrodes, offer high power densities [1,2]. They are attracting increasing interest and are showing growing promise in automotive, personal electronics, and grid-scale electrical energy storage systems [3]. The charge storage mechanism of supercapacitors facilitates rapid charge transport and is more efficient than transport-limited redox and intercalation processes of

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traditional batteries. Subsequently, they offer up to 15 kW kg<sup>-1</sup> power densities and a very large operating cycle life. However, the electrosorption process is not energy-dense and can offer only 6 Wh kg<sup>-1</sup> [4]. Many applications, such as wearable electronics or hand-held devices, require supercapacitors with high volumetric capacitance and large areal electrode mass loading [5,6]. Since energy density is exponentially dependent on applied potential, the next generation of supercapacitors must rely on electrode and electrolyte combinations that exceed the current ~2.7 V window limit [7]. Finally, the material costs of electrochemical capacitors must remain low for them to become viably competitive with batteries, fuel cells, and other energy storage systems.

Existing commercial supercapacitors predominantly implement activated carbon with the particle size of a few microns. It is commonly derived from biomass (coconut shells, wood char, or peat bog) using chemical or physical activation at 800–900 °C [8]. Carbide derived carbons (CDCs), which are synthesized *via* Cl<sub>2</sub> (g) etching of metal carbides (TiC, SiC, Mo<sub>2</sub>C, B<sub>4</sub>C, etc.) at 200–1200 °C, offer high specific surface areas (1000–2000 m<sup>2</sup> g<sup>-1</sup>) and tunable [9], monodisperse porosities [10,11]. Since their pore diameter (5 Å <  $d_{pore}$  < 11 Å) can be selected to match the size of electro-sorbed ions, CDCs have demonstrated exceptional capacitance of over 150 F g<sup>-1</sup> in non-aqueous electrolytes [12,13]. Furthermore, their thermal and electrochemical stability makes them a promising supercapacitor carbon alternative [10]. Stemming from high porosity of these materials, the Cl<sub>2</sub> + metal carbide reaction proceeds at a linear rate (for grains <80 μm thick) with minimal transport limitations [14]. From CDCs that had been analyzed in electrochemical capacitors, those derived from TiC precursors (TiC-CDCs) have subnanometer pores and offer the highest charge storage densities [15]. However, similar to other well-tuned internal pore structures (such as templated mesoporous carbons and activated graphene), CDC synthesis process has not been sufficiently cost-effective for these materials to become economically competitive with activated carbon. At the same time, they offer an excellent model system for studying fundamental aspects of charge storage in porous carbons.

A viable approach that improves the scalability of CDC synthesis minimizes the cost of carbide precursors. Since carbides undergo a conformational transformation during synthesis [16], their starting dimensions are identical to those of desired CDC particles (1–5 μm diameters). Prolonged milling and sieving, which is required to produce micron-sized TiC powders, makes them significantly more expensive than coarse, abrasive carbide powders. Other previously reported supercapacitors, which were composed of nanosized CDC electrode particles [17], had relied on high-energy plasma synthesis of 20 nm TiC precursor nanopowders [18]. If future supercapacitor electrodes can successfully implement coarse-grained, large carbon (CDC or activated carbon) electrodes, these devices will become much more economically viable. However, all commercial devices use small carbon particles and a previous study on SiC-CDC [19] showed that capacitance increases with decreasing particle size in the range from 30 nm to 20 μm. No attention has been paid to larger particles, as it has been known that long pore lengths may impede ion mobility [19–23]. However, recent *in situ* FTIR spectroelectrochemistry experiments have shown that electrosorption predominantly involves short-range interactions (<10 nm), and bulk transport of electrolyte across the cell is not a rate-limiting step [24]. Furthermore, we have demonstrated rectangular cyclic voltammograms (CV) high charge storage densities and good rate handling abilities in flow supercapacitor cells, which rely on a slurry suspension of granular (100–200 μm) microporous activated carbon beads [25,26]. The latter work underscores the importance of a good electron transport network through the electrode, and shows that large particles may deliver high capacitance. However,

those powders were suspended in electrolyte – a different arrangement compared to polymer-bonded electrode films. Monolithic TiC-CDC films showed excellent capacitance [27,28], but this result could not be scaled to thicker CDC plates (250 μm thicknesses) [29,30].

Our objective is to study capacitance and rate handling capabilities of coarse-grained porous carbon powders in supercapacitors. Our approach relies on commercial-grade abrasive TiC powder, which is significantly less expensive than microscale or nanoscale powders, with minimal synthesis and processing steps. We demonstrate superior performance of resulting electrode films in different electrolytes compared to conventional activated carbons. From a fundamental perspective, this finding highlights the significance of short-range interactions and stresses the importance of development of novel charge electrosorption models. We demonstrate that ion behavior in narrow, confined pores is significantly different than that of double layer adsorption on flat, external surfaces [31,32]. In addition to greater capacitance, electrochemical stability of ions may improve due to minimized external surface and maximized confinement in narrow pores. Finally, porous particles with long and interconnected pores provide us with a novel model system to evaluate the influence of pore wall chemistry on capacitance and ion mobility. From a practical perspective, we introduce high-performing carbon electrodes with superior mass loading, gravimetric and volumetric energy densities, and reduced cost.

## 2. Experimental methods

### 2.1. Materials synthesis

The starting precursor material for all experiments was TiC powder (Reaktiv, Donetsk, Ukraine) with a 140–250 μm particle size. A ball mill ground up the material for 15 h (HDPE enclosure, TiC grinding media). A Ro-Tap particle sieving instrument separated the fraction containing 40–80 μm particles. TiC was converted to TiC-CDC according to a previously described procedure [33,34]. Particles were pelletized with polyvinyl acetate (PVA), loaded into a quartz boat, and placed into a horizontal tube furnace. A boat filled with activated carbon was placed in front of the TiC-containing one to remove oxygen or other impurities in the gas stream. The material was heated to 800 °C under a flowing Ar atmosphere (198 cm<sup>3</sup> min<sup>-1</sup>). Subsequently, it was treated with Cl<sub>2</sub> (g) (370 cm<sup>3</sup> min<sup>-1</sup>) at 800 °C for 6.5 h and H<sub>2</sub> (g) (492 cm<sup>3</sup> min<sup>-1</sup>) at 600 °C for 2 h. The material was cooled under flowing Ar, removed, and weighted. Photographs of the boat before and after synthesis are shown in Fig. S1 in Supplementary Information (SI). This coarse powder material was used for the majority of the testing and is also referred to as “Initial CDC.” Additionally, some 250 μm diameter TiC particles were converted to CDC using the same procedure without any milling. They are referred to as “Large CDC.” For comparison of basic material properties and electrochemical performance, we used YP50 activated carbon (Kuraray, Okayama, Japan) and TiC-CDC and SiC-CDC micro- and nanopowders that were synthesized using the same method as described above.

Approximately 500 mg of initial CDC material was manually ground up in an agate mortar and pestle for 2 h. Water and ethanol were intermittently used to facilitate the pulverization process. The smaller-particle variant of the CDC powder is hereafter referred to as “Milled CDC.”

### 2.2. Materials characterization

A Quadrasorb gas sorption analyzer (Quantachrome

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