Power-Limiting Role of Internal Resistance in MnO_2-Graphitic Carbon Pseudocapacitors

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Despite the promising synergetic properties of MnO_2 – a low cost, high specific energy material – with graphitic carbon – an electrochemically stable, high specific power material – the MnO_2-graphitic carbon pseudocapacitor has yet to achieve its full potential in terms of both specific energy and specific power. Improving the properties of MnO_2-carbon composites for practical devices requires developing and understanding of the mechanisms limiting their performance.

To better understand power-limiting mechanisms in MnO_2-carbon composites, have fabricated a series of comparative nanoscale devices using single, isolated single-walled carbon nanotubes (SWNT), multi-walled carbon nanotubes (MWNT), or lithographically patterned Pt as the collector electrodes (Fig. 1, top). The SWNT and MWNT electrodes were engineered such that only a 1 μm length of any selected nanotube was exposed to a MnO_2 plating solution. Conformal films of highly porous, delta-phase MnO_2 was then deposited by pulsed electrochemical deposition.

Devices having a range of geometries were characterized using cyclic voltammetry to extract specific capacitances and resistances for each type of electrode. The specific capacitance was well behaved and reproducible for the entire set of samples. In fact, down to sub-picogram quantities of MnO_2 deposited on a single SWNT, the specific capacitances agreed remarkably well with bulk measurements (Fig 1, middle).

Series resistance, on the other hand, varied widely for nominally-identical MnO_2 films. Multiple mechanisms contribute to this resistance, including charge transfer at the electrolyte-MnO_2 interface, Li+ ion diffusion, MnO_2 electronic transport, and charge transfer at the MnO_2-collector interface. Attempts to separate the contribution of each focused on distinguishing the lowest-resistance Pt collector from the highest-resistance, prisitine SWNT collector. Ultimately, though, the scan rate dependencies masked obvious differences due to the electronic components. In fact, RC time constants reproduced even in the limit of a 10^9 MnO_2:C ratio and a 1000 A/m^2 current density at the MnO_2-SWNT interface. Thus, by scaling down the MnO_2-graphitic carbon system to the smallest of its constituents, we have placed an upper limit on the possible role of electronic MnO_2-carbon interface in these composite pseudocapacitors.

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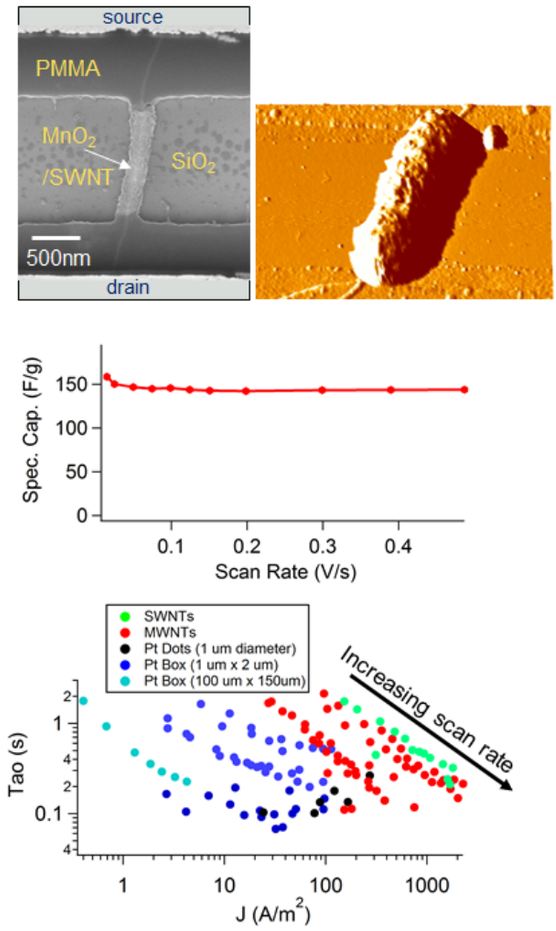

Fig 1. (top) An example SEM and AFM image of individual single-walled carbon nanotube MnO_2 pseudocapacitors. (middle) A typical plot of specific capacitance versus scan rate (15mV/s to 500mV/s) shows that little pseudocapacitance even at slow scan rates. (bottom) The charging time constants for various working electrodes, for a given scan rate, is independent of working electrode size and chemistry, even for current densities of 1000 A/m^2.