A Mixed Mathematical and Experimental Model for Energy Storage in Electrospun Mn_2O_3 Supercapacitor Electrodes

M. Brockway, J.L. Skinner
Montana Tech Nanotechnology Laboratory, Montana Technological University, Butte, MT 59701
mbrockway@mtech.edu

Supercapacitors are a developing technology for use with renewable energy, hybrid and electric vehicles, and personal electronics. Supercapacitors combine the high energy density of batteries with the power density of capacitors, bridging the gap between the two technologies.[1] Nanostructures provide ultrahigh specific surface area to supercapacitor electrodes, thereby increasing energy storage sites and specific capacitance. Traditionally fabricated nanostructured electrodes are produced by mixing active materials with binders and conductive agents and pasting onto charge collectors. Previously, we have reported a facile fabrication process wherein Mn_2O_3 is electrospun directly onto charge collectors to produce freestanding, web-based supercapacitor electrodes with increased accessible surface area.[2] Herein, we combine experimentally determined supercapacitor cell parameters with theoretical mathematics to produce a model describing the effects of electrode morphology and structure on energy storage capacity.

While detailed models exist for supercapacitor energy storage in nanostructured RuO_2 and carbon-based electrodes,[3,4] Mn_2O_3 has not been as well-examined despite its promise as a low-cost supercapacitor electrode material. Additionally, the unique structure of porous electrospun web electrodes has not yet been modeled. By producing a model to describe the effect of active material, fiber size, and electrode porosity on the performance of freestanding web electrodes, ideal parameter values can be determined to improve low-cost, high performance electrodes.

This work combines experimentally measured system and material parameters with mathematical theory to produce a charge storage model that closely mimics actual energy storage. Experimentally collected data serves as the starting point for model derivation, thus ensuring the model captures all present energy storage and leakage processes. Time constants, effective capacitance, and capacitance due to adhesion and Faradaic processes are calculated from electrochemical impedance spectroscopy (Fig. 1). Fiber size and packing density are measured from scanning electron micrographs (Fig. 2A), and fiber porosity is examined with transmission electron microscopy (Fig. 2B). The measured and calculated parameters are combined with literature and assumed values to produce a model describing energy storage in the Mn_2O_3 web electrodes.

[1] Simon, P. Gogotsi, Y. Dunn, and Bruce, Sci. Mag. **343**, 1210 (2014). [2] M. Brockway and J. Skinner, J. Vac. Sci. Technol. B **38**, 62401 (2020). [3] C. Lin, *et. al* J. Electrochem. Soc. **146** (1999). [4] J. Huang, B.G. Sumpter, and V. Meunier, Chem. Eur. **14** (2008).

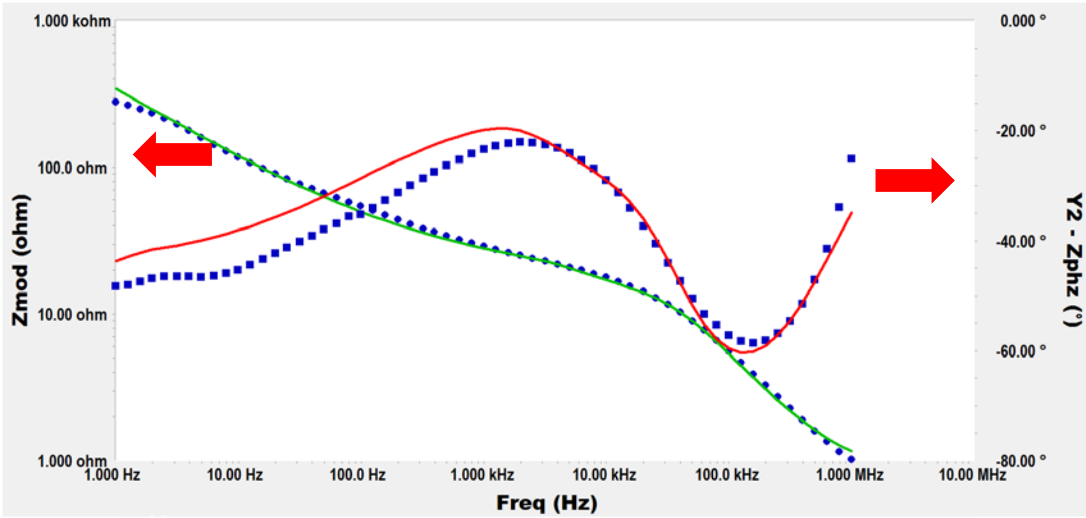

Figure 1: Bode plot of electrochemical impedance spectra collected (dots) for a Mn(III) oxide web electrode with equivalent circuit model (lines) applied. Equivalent circuit model shows good agreement with experimental data.

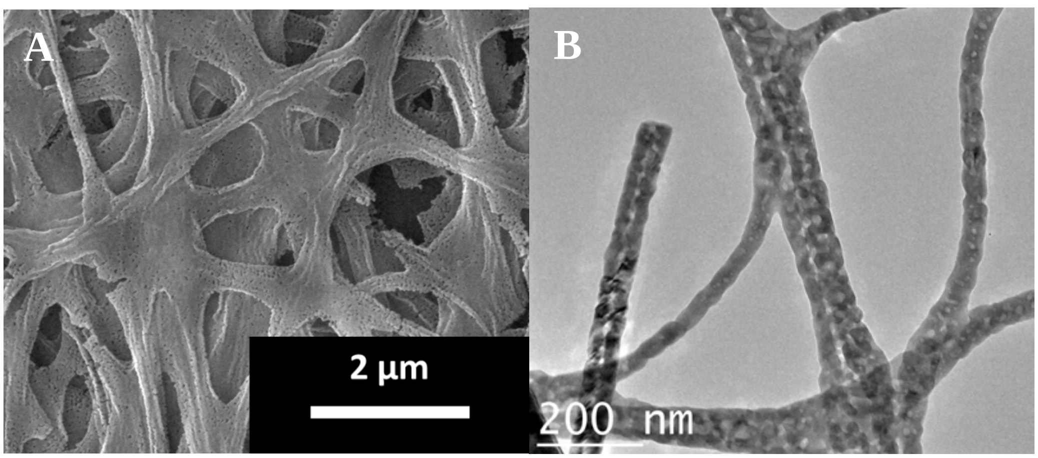

Figure 2: Scanning electron micrograph **(A)** and transmission electron micrograph **(B)** of electrospun web electrode showing porous interconnected structure and fiber size. Fiber morphology is shown to affect electrochemical properties of resultant electrodes.