

## Solid-State Nano-composite Supercapacitors

Se-Hee Lee, Yanfa Yan, C. Edwin Tracy, J. Roland Pitts, and Satyen K. Deb

*National Renewable Energy Laboratory  
1617 Cole Boulevard, Golden, CO 80401*

The electrochemical capacitor (ECC) is an attractive device for high power density applications. When working together with secondary batteries, electrochemical capacitors provide additional versatility and efficiency in the management of portable power sources. There are two known energy-storage mechanisms in ECC. The double-layer (DL) storage mechanism involves charge separation at the electrode/electrolyte interface, while the faradaic redox reaction at the surfaces gives rise to the "pseudocapacitance or supercapacitance."<sup>1</sup> Commercially available high surface carbon materials such as activated carbon, activated carbon fiber cloth, and carbon aerogel/foams are commonly used as electrodes (in liquid/gel electrolytes) to fabricate double-layer capacitors with increased specific capacitance.<sup>2</sup> However, these non solid-state capacitors suffer from the incomplete use and inaccessibility of the total surface due to the fact that a significant fraction of micropores ( $\leq 2$  nm) cannot be wetted by the electrolyte.<sup>3</sup> Furthermore, their inherently high internal resistance limits the function of this type of capacitor to only low-current applications.<sup>4</sup>

Some transition metal oxides, such as  $\text{RuO}_2$  and  $\text{IrO}_2$  have been shown to exhibit promising properties as supercapacitor materials. An amorphous phase of  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  formed by the sol-gel method at low temperatures shows a specific capacitance as high as 720 F/g in an acidic electrolyte<sup>5</sup> but the high cost of these materials detracts from its commercialization. Hence, much effort has been expended in searching for alternative electrode materials (e.g., nickel oxide, cobalt oxide, and manganese oxide)<sup>6-8</sup> which are inexpensive and exhibit pseudocapacitive behavior similar to that of  $\text{RuO}_2$  and  $\text{IrO}_2$ . However, these alternative materials also suffer from electrolyte wetting problems especially when small particle sizes are employed.

The search for a totally solid-state (non liquid/gel electrolyte) supercapacitor is a subject of current research. In this paper we report on the development of extremely small particle size nano-composite materials for solid-state supercapacitor applications. Because of the rapid advance in the development of electronic devices, such as portable computers, cellular phones, pagers and the latest developments in electric vehicles, there is a need for further improvements in their power sources. A solid-state power source commands the advantage of being free of liquid leakage and exhibits a decrease in both self-discharge and leakage current. Consequently, a solid-state power source is safer and has more forgiving packaging requirements than its liquid counterpart. This is especially important in the application of electronic devices and electric vehicles. The polycrystalline/amorphous nano-composite structure that we have synthesized is ideal for use as a solid-state supercapacitor for two primary reasons: one, because it allows nano-particles with a large surface area to generate a high specific capacitance, and two, the solid-state proton electrolyte intimately surrounds the nano-particles which increases the usage and accessibility of the total particle surface.

Thin film nano-composites of polycrystalline nickel oxide/amorphous tantalum oxide electrolyte were deposited by reactive RF-magnetron sputtering in  $\text{O}_2$  from a composite target. The thin films were prepared on indium tin oxide (ITO) coated glass for optical transmittance and electrochemical measurements and on polished stainless steel substrates for x-ray diffraction analysis, Raman spectroscopy, and TEM measurements. The composition of these nano-composites was evaluated by X-ray photoelectron spectroscopy (XPS) analysis and inductively coupled plasma (ICP) spectrometry. The average size of the nickel oxide nano-particles was adjusted by varying the RF sputtering power and the working pressure. The compositional ratio of the composite was adjusted by changing the surface ratio of the tantalum arrayed nickel target. The electrochemical characteristics of the resulting nano-composite  $\text{NiO}/\text{Ta}_2\text{O}_5$  electrodes was examined in NaCl aqueous solutions using cyclic voltammetry as well as AC impedance spectroscopy.

## References

1. B. E. Conway, *J. Electrochem. Soc.*, 138, 1539 (1991).
2. J. M. Miller, B. Dunn, T. D. Tran, and R. W. Pekala, *J. Electrochem. Soc.*, 144, L309 (1997).
3. S. T. Mayer, R. W. Pekala, and J. L. Kaschmitter, *J. Electrochem. Soc.*, 140, 446 (1993).
4. K. C. Liu and M. A. Anderson, *J. Electrochem. Soc.*, 143, 124 (1996).
5. J. P. Zheng, P. J. Cygan, and T. R. Zow, *J. Electrochem. Soc.*, 142, 2699 (1995).
6. E. E. Kalu, T. T. Nwoga, V. Srinivasan, and J. W. Weidner, *J. Power. Sources*, 92, 163 (2001).
7. C. Lin, J. A. Ritter, and B. N. Popov, *J. Electrochem. Soc.*, 145, 4097 (1998).
8. S. C. Pang, M. A. Anderson, and T. W. Chapman, *J. Electrochem. Soc.*, 147, 444 (2000).