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Pseudocapacitor with High Energy & Power Densities Based on Nickel Oxide Nanostructures

We developed a simple and commercially viable procedure to fabricate supercapacitors electrodes based on NiO/Ni nanocomposites. By developing a slow charge and fast discharge process, high energy and power densities of 60 Wh/kg and 10 kW/kg were achieved simultaneously.
**Award Information**

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<tr>
<td>Title</td>
<td>Supercapacitor with High Energy and Power Densities Based on NiO Nanostructures</td>
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<tr>
<td>Principal Investigator</td>
<td>John Q Xiao</td>
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<td>Organization</td>
<td>University of Delaware</td>
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**Technical Section**

**Objective**

To develop supercapacitors based on NiO or other oxides nanocomposite electrodes and appropriate electrolytes to achieve specific capacitance (SC) of 400 F g\(^{-1}\), energy and power densities of 50 Wh kg\(^{-1}\) and 10 kW kg\(^{-1}\), respectively.

**Approach**

Our initial effort has been focused on the science of the electrochemical properties of NiO in order to guide our electrode and electrolyte designs. The studies include poly-crystalline and single-crystalline mesoporous nickel oxide; crystalline and amorphous NiO films of different thicknesses, and their associated supercapacitor performance in both acidic and alkaline electrolytes. In the meantime, we have developed a low-cost technique to fabricate monolithic Ni/NiO core/shell nanocomposite electrodes in aqueous KOH electrolyte to achieve the proposed objective.

**Progress**

1. **Demonstration of Enhanced Supercapacitor Performance by Controlling Electrode Crystallinity**

   In order to demonstrate the importance electrode crystallinity for high-performance supercapacitor, poly-crystalline and single-crystalline mesoporous nickel oxide electrodes (Figure 1a-c) have been synthesized and characterized for supercapacitor application. Both electrodes exhibited well-defined 3D pore network with similar pore sizes and surface area (Figure 1d, e), however, the polycrystalline electrodes are superior over the single crystalline electrodes by providing more charge storage in electrode bulk, achieving a factor of 10 higher specific capacitance (SC) of 356 F g\(^{-1}\). This is the first demonstration that oxide materials with similar ordered pore structure and surface area but different crystallinity exhibit a large variation in charge capacity.

![Figure 1](image_url). XRD, ED patterns and TEM images for single-crystalline (a upper panel, b and d) and polycrystalline (a lower panel, c and e) mesoporous nickel oxide.
2. Differentiation of Bulk and Surface contribution to super-capacitance in amorphous and crystalline NiO

In order to obtain a more quantitative insight of how electrode crystallinity affects the charge storage, we recently investigated a model system based on NiO thin films with well-defined column structures and controlled crystallinity (Figure 2). The specific capacitances contributed from electrode surfaces and electrode bulk were differentiated by separating the cyclic voltammometric curves into a capacitive portion and a diffusion controlled portion from which we drew the important conclusion that the specific capacitance from surface contribution is the same for both amorphous and crystalline films, however for the same surface area, the specific capacitance from bulk contribution should be at least three times larger in amorphous films than in crystalline films.

![Figure 2. XRD patterns, TEM and AFM images of amorphous (a blue curve, c and e) and crystalline NiO thin film (a red curve, d and f). Typical cyclic voltammetric (CV) curves of NiO in ideal capacitor region (b upper panel) and in the region including redox reactions (b lower panel).](image)


The process started with the production of nickel nanoparticles by reducing Ni2+ ions in high-boiling temperature polyalcohols (Figure 3a). The obtained nanoparticles were mechanically compressed into pellets to form porous prototype electrodes (Figure 3b, c), of which the pore size was optimized by controlling the size of Ni nanoparticles. A very thin platinum coating was deposited onto one side of the pellet which later acts as a current collector. Annealing at different thermal conditions forms a layer of nickel oxide around the porous nickel network which serves as the functional material. The thickness of nickel oxide layer and its crystallite sizes can be tuned for simultaneous achieved high electrode conductivity and small crystallinity. The resulting nanocomposite electrodes are highly porous, mechanically stable and do not require any further support or additives.
Figure 3. Characterization of the electrode structure: a) TEM image and ED pattern of the as-prepared Ni nanoparticles. SEM images at the b) surface and c) cross-section of the prototype electrode. Characterization of the conductivity and crystallinity: d) Resistivities of samples prepared at different thermal conditions. Inset: I-V curves and associated linear fits within the range of -0.1 to 0.1 V. At 250 °C the sample behaves like a metal, whereas at 350 °C it shows a tunneling effect because of the isolated conductive metal cores. e) ED patterns of the NiO/Ni nanoparticles oxidized at different temperatures.

The electrodes prepared at 250 °C exhibited a high conductivity with metallic behavior and very fine nickel oxide particle sizes (Figure 3d, e). As intentionally desired, the resulted large specific capacitance of 910 F g\(^{-1}\) was not only better than that of their higher temperature counterparts, but was among the best values achieved in the field of supercapacitor. By developing a slow charge/fast discharge process (Figure 4a), a probably state-of-art supercapacitor performance of both high energy density of about 60 Wh kg\(^{-1}\) and high power density of 10 kW kg\(^{-1}\) was simultaneous achieved (Figure 4b).

Figure 4. Slow charge and fast discharge characterization. a) Cyclic chronopotentiometric curves with charge current density of 1 A g\(^{-1}\) and various discharge current densities. b) Ragon plot (power density vs. energy density) derived from discharge curves of a).
4. **Demonstration of FeO\textsubscript{x} as Promising Counter Electrode Material**

In order to increase the voltage window and further improve the energy density and power density, we demonstrated FeO\textsubscript{x} as promising counter electrode material to couple with Ni/NiO nanocomposite electrodes, which could extend voltage window from 0.7 V to 1.65 V. Figure 5 shows the CV curve of FeO\textsubscript{x} thin film obtained from sintering a 20 nm thick Fe film in atmospheric air at 200 °C. The specific capacitance derived from associated CV curve is about 750 F g\textsuperscript{-1}, and is comparable with that of Ni/NiO nanocomposite electrodes. If its fabrication procedure could also be applied for achieving Fe/FeO\textsubscript{x} nanocomposite electrodes, the energy density of the full asymmetric supercapacitor (normalized to all electrodes masses) is estimated to be close to 20 kW kg\textsuperscript{-1} at a power density of about 10 kW kg\textsuperscript{-1}.

**Summary**

We have developed procedures to fabricate high conductive Ni/NiO electrodes with high energy and power density. With similar procedures, we will develop Fe/FeO\textsubscript{x} counter electrode to increase the operating potential window. The objectives have been delivered at the end of this program.

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**Cumulative Statistics**

**Documentation / Publications**

1. Qi Lu and John Q Xiao “How to Design Nanostructured Supercapacitor Electrodes for High-performance Supercapacitors” submitted to Chemphyschem. (Invited Review)
**Conference presentations/proceedings**


**Invention disclosures/patents**

- Pending provisional patent: Fabrication of Metal and Oxide Nanofiber and Porous Structure
- Invention disclosure in preparation: High-Energy and -Power Density Electrodes for Electrochemical Capacitors Prepared from Monolithic Metal Oxide/Metal Nanocomposite

**Students/Postdocs supported by this award**

- *Graduate students*: Daniel Esposito (partially), Qi Lu, Zach Mellinger, Xing Chen, and Yunpeng Chen

**Other noteworthy recognition**

- Qi Lu: Received Daicar-Bata Prize for the best research paper in Physics and Astronomy Department, University of Delaware 2011.
- Daniel Esposito: Received NASA Graduate Fellowship
- Jingguang Chen: Received 2008 Excellence in Catalysis Award sponsored by the NY Catalysis Society; Elected Fellow by AVS; Received Named Professorship (Claire D. LeClaire) from UD.