

Increased electricity storage and faster delivery

Electrochemical electrode material with combined supercapacitor and battery behaviors

The advancements of mobile electronic devices have increased the demand for energy storage devices with not only high storage capacity but also fast power performance. Supercapacitors are capable of delivering fast power with both high coulombic and energy efficiencies; however, the charge-storage capacities of supercapacitors are substantially lower than those of batteries. The conventional strategy to combine supercapacitors and batteries involves making electronic hybrid systems that fulfill the energy and power requirements of modern high-technology devices. One of the recent focuses in the Energy Materials Laboratory (EML) led by Professor Nae-Lih Wu in the Department of Chemical Engineering is the exploration of novel bifunctional electrode materials that simultaneously exhibit supercapacitor and battery behaviors and enable the advantages of supercapacitors and batteries to be achieved in a single electrochemical charge-storage cell.

One example of a bifunctional electrode material is a tailored $\text{SiO}_2\text{-MnO}_2$ nanocomposite synthesized via a facile hydrothermal process. MnO_2 is an attractive pseudocapacitive electrode material because of its low cost, natural abundance, and environmental friendliness. The use of aqueous MnO_2 -based pseudocapacitors has been limited to a small operating voltage window of approximately 1 V, and the electrode exhibits purely capacitive behavior with a limited charge-storage capacity. The operating voltage window is mainly limited by the structural instability of the oxide caused by an irreversible phase transformation and loss of the active material via dissolution toward the lower voltage limit.

Dr. Yu-Ting Weng of the EML derived a new material design strategy to extend the electrochemical stability of the MnO_2 electrode over a substantially widened operating voltage window. This strategy was based on the concept of forming space-con-

fined MnO_2 nanodomains of which the surfaces are stabilized using an electrochemically inactive foreign oxide material, such as SiO_2 , that can restrain the phase change of the MnO_2 nanodomains and suppress interface erosion. Spherical mesoporous SiO_2 nanobeads were used as hosts for the deposition of MnO_2 via a hydrothermal process, facilitating the formation of Mn–O–Si composite interfaces.

The electrochemical behavior of the resulting nanocomposite material, which exhibits a 2 V-operating window ($-1.0 \sim 1.0$ V versus Ag/AgCl reference), is schematically described in Figure 2. The pseudocapacitance originating from Mn(IV)-Mn(III) charge transfer, denoted as PC (IV)-(III), occurs between 0 and -1 V. Pseudocapacitance from the Mn(III)-Mn(II) redox reaction, denoted as PC (III)-(II), commences below 0 V. The battery behavior involving the bulk reduction of Mn(IV) to Mn(II) and then to Mn(II), denoted as B (IV) \rightarrow (III)

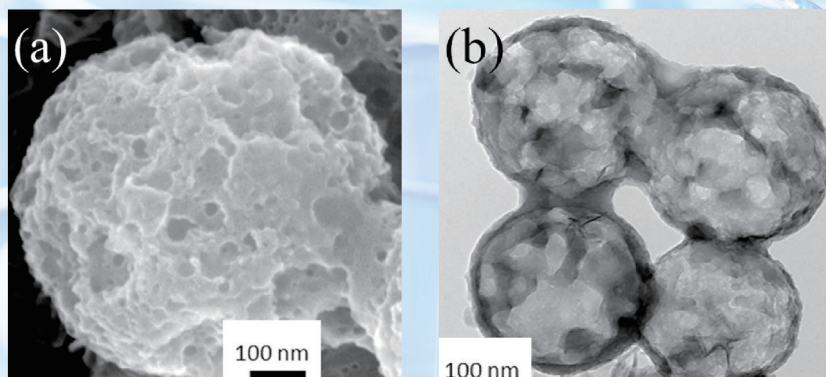


Figure 1. Scanning (a) and transmission (b) electron micrographs revealing the microstructures of the derived nanoporous $\text{MnO}_2\text{-SiO}_2$ spheres.

and B (III)→(II), respectively, occurs primarily between 0 and -1 V. However, the battery behavior involving oxidation from Mn(II) to Mn(III) and then to Mn(IV), i.e., B (II)→(III) and B (III)→(IV), respectively, concurrently occurs with PC (IV)→(III) from -0.3 to 1 V. The figure also illustrates that the battery behavior provides a substantial amount of charge-storage capacity in addition to pseudocapacitance at low scan rates. This study suggests a new strategy to design and develop new electrochemical electrode materials for more efficient energy storage and wider applications.

Reference

Yu-Ting Weng, Hsiao-An Pan, Rung-Chuan Lee, Tzu-Yang Huang, Yun Chu, Jyh-Fu Lee, Hwo-Shuenn Sheu and Nae-Lih Wu, (2015). Spatially Confined MnO₂ Nanostructure Enabling Consecutive Reversible Charge Transfer from Mn(IV) to Mn(II) in Mixed Pseudocapacitor-

Battery Electrode. *Advanced Energy Materials*, 5, 1500772. DOI: 10.1002/aenm.201500772.

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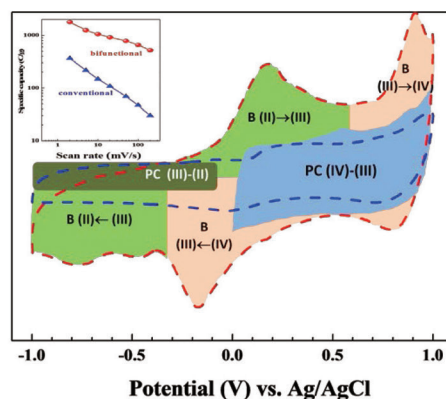


Figure 2. Schematic of the various charge-storage mechanisms as a function of potential; B: battery behavior; PC: pseudocapacitance; (IV), (III) and (II): Mn ions with a valence of 4, 3 and 2, respectively. The inset compares the charge-storage capacities between the bifunctional MnO₂-SiO₂ composite electrode (red) and a conventional MnO₂ electrode (blue).

Post lithium-ion batteries: lithium-sulfur batteries

Probing the discharge and charge mechanism of lithium-sulfur batteries

The ever-rising demand for portable power sources has prompted a renewed interest in next-generation energy storage systems, including batteries, fuel cells and electrochemical capacitors. The applications of these energy storage devices range from consumer electronics to next-generation electric vehicles. Among the various energy storage technologies, batteries are by far the most successful products in the consumer market.

Although Li-ion batteries (theoretical specific energy of C/LiCoO₂ is ~387 Wh kg⁻¹) still dominate the portable electronic device market, their capacity cannot reach the requirements of batteries for electric vehicles. Next-generation Li batteries, such as Li-S batteries, have attracted attention recently, mainly due to their low cost and high theoretical specific energy of ~2567 Wh kg⁻¹. However, many problems associated with the battery performance, such as

dendrite formation at the Li anode and dissolution of intermediates from the S/C cathode, still limit the practical application of Li-S batteries.

To overcome these technical challenges regarding Li-S batteries, a detailed understanding of the discharge/charge mechanism is needed, as all the electrochemical reactions occurring on the cathode and anode are based on the fundamentals of electrochem-