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CPCPC Success Story

Asymmetric Electrochemical Capacitor Derived from Coal

Collaborators: University of Kentucky Center for Applied Energy Research, Jeddo Coal Company (Pennsylvania)

Description: Electrochemical double-layer capacitors (EDLCs), often referred to as supercapacitors or ultracapacitors, are electrochemical energy storage devices capable of storing and delivering energy at higher rates than most batteries including advanced Li-ion. Electrochemical capacitors typically possess lower energy densities than batteries, but have many advantages, including higher power densities (i.e. rapid charge and discharge), extended cycle life and undergo no chemical or structural changes during charge and discharge. Typical electrode materials for supercapacitors are based on activated carbons, which are characterized by high surface area, and a porous structure that allows electrolytes to infiltrate into the pore volume. High surface area is desired, as capacitance, C is directly proportional to the surface area, A, of the carbon ($C = ke_o(A/d)$), where e_o is the dielectric constant of the medium between the parallel plate electrodes and d is separation between the electrodes. Activated carbons are typically prepared by either physical (i.e. steam or CO_2) or chemical activation, where the carbon precursor is mixed with chemical agents such as KOH or $ZnCl_2$ and heated to high temperatures under an inert atmosphere to produce micro- and meso-pores. Through sponsorship of the CPCPC, one carbonaceous material under investigation at the CAER is bituminous and anthracite coal. By simply exposing coal (in ground form) to steam at 900 ^{o}C for 20 minutes or less, porous carbons suitable as active materials for electrochemical capacitors can be prepared. Energy densities exceeding 120 Fg-1 in both lithium nitrate and sulfate electrolytes have been achieved for coal-derived carbons, including activated coal tar pitch fiber. Further enhancement in the energy density is expected with improved activation processes and electrode/electrolyte wetting.

Porous carbons derived from coal are used as electrode materials in a novel asymmetric electrochemical capacitor using aqueous electrolyte. The capacitor uses a lithium-doped manganese spinel electrode as the positive and an activated coal carbon as the negative. Lithium nitrate serves as the electrolyte. The capacitor operates by the insertion and extraction of Li ions in the manganese spinel lattice during discharge and charge, respectively while the activated carbon electrode stores charge through Li^+ and anion adsorption/desorption. The asymmetric system uses low-cost, environmentally benign, nontoxic electrode materials and mild electrolyte (4M $LiNO_3$). The operating cell voltage of the capacitor is over 2V, with an estimated gravimetric energy density of about 25 Whg^{-1} based on active materials only. The Li manganese spinel/carbon capacitor can compete with other aqueous based systems, like the lead dioxide/sulfuric acid/carbon capacitor currently under commercial development in the United States and Russia. The Li manganese spinel/carbon system has several advantages over the PbO_2/carbon capacitor in that it uses nontoxic materials and electrolyte, has a higher cell operating voltage (> 2.1) and involves solid-state ion transport as the storage mechanism for the positive electrode resulting in no phase change during charge and discharge. The asymmetric Li manganese spinel/$LiNO_3$/carbon capacitor is represented schematically in Figure 1.

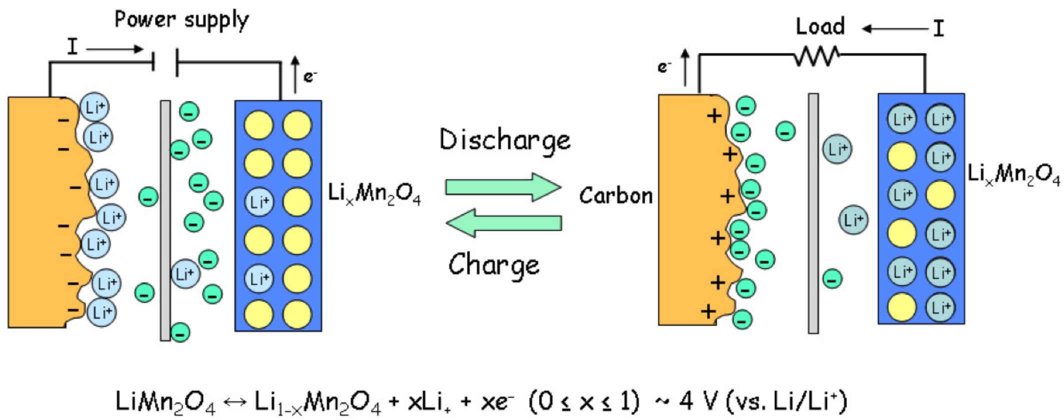

Figure 1. Operation mechanism of asymmetric capacitor using Li-ion intercalation positive and coal-derived carbon negative electrodes.

The coal-derived carbons have also been investigated as active electrode materials in organic-based electrolyte systems. Results thus far have shown that activated coal-derived carbons with relatively low surface area (S_{BET} ~ 800 m^2g^{-1}) can achieve energy densities close to 100 Fg^{-1} in organic electrolytes like 1.8M $TEMABF_4$. Additionally, rate performance for porous coal-derived carbons is excellent as they maintain respectable power densities at charge/discharge rates up to 2.5 Ag^{-1}. Electronic conductivities for steam-activated coal are also very good and, in most cases, little if any conductive additives are required in the fabrication of electrodes.

The carbon capacitor development effort supported by the CPCPC has been instrumental in promoting additional capacitor carbon research activities as the CAER recently obtained $515k in funding from the Office of Naval Research. This work involves the development of an organic-based asymmetric capacitor, which will be used in combination with a metal/air battery (i.e., a hybrid power source) to provide power for portable Marine electronic systems. This capacitor technology will use graphitic lithium-ion intercalation and porous carbon electrodes to develop a 4V capacitor. The primary goal is to create a safe, compact, lightweight and longer-lasting power source to meet future Marine Corp mission requirements, which demand improved power and energy performance.

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