

Novel Hybrid Aqueous Supercapacitor

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High surface area MnO₂ has been recently proposed as active electrode material for electrochemical supercapacitor. These electrodes exhibited a pseudo-capacitive behavior with specific capacitance ranging from 100-200 F/g for powder-based electrodes (1) to 600 F/g for thin films (2) within a 0.9-1.2V potential window in mild aqueous electrolytes based on KCl, K₂SO₄ or Na₂SO₄. Despite that MnO₂ is a low-cost material and environmentally friendly, the potential window over which it could be used is too small compared to organic based supercapacitors to envision the design of a supercapacitor using two MnO₂ electrodes.

Figure 1a shows that the cyclic voltammogram of a MnO₂ electrode in aqueous K₂SO₄ is characterized by a reduction wave at about 0 V in neutral pH electrolytes. This reduction process is related to the onset of the formation of MnOOH which is the faradaic reaction taking place in alkaline primary batteries. Therefore, the MnO₂ potential window cannot be extended toward lower potential. At the positive potential limit, the onset of the oxygen evolution reaction occurs at 1.2V. Thus, the limiting factor for increasing the potential voltage of a MnO₂ based supercapacitor in neutral aqueous electrolyte is clearly related to redox processes that are not involved to the charge/discharge reaction of MnO₂. Subsequently, it can be envisioned to build a hybrid system with a positive MnO₂ based electrode and a negative electrode which presents an high overpotential for the hydrogen evolution reaction. Such a negative electrode should also fit the requirements of good specific capacitance value in mild aqueous media and limited cost. Figure 1b indicates that activated carbon electrode fits the previous requirements. A recent paper (3) described such a hybrid system working at an operating voltage of 2 V in KCl electrolyte. However, the cycling stability was only shown for 100 cycles and the problems related to gas evolution at the electrodes were not addressed in detail.

In this study, we report the electrochemical behavior of a hybrid supercapacitor using activated carbon as the negative electrode and composite MnO₂ electrode as the positive electrode in a mild aqueous electrolyte (0.65 M K₂SO₄, pH = 6.5). A cell based on these two electrodes was designed and operated at different charge/discharge currents and a potential of 2.2V without noticeable gas evolution (Figure 2). Additionally, the hybrid device has shown a good cycling behavior at a constant power of 1.2 kW/kg (of active material) as shown in Figure 3.

Further investigations are required to optimize the MnO₂/AC hybrid supercapacitor, especially the correct determination of gas evolution at both electrodes as well as the analysis of the energy fade upon cycling. However, this hybrid system opens the way for new competitive low cost devices working in neutral aqueous electrolytes.

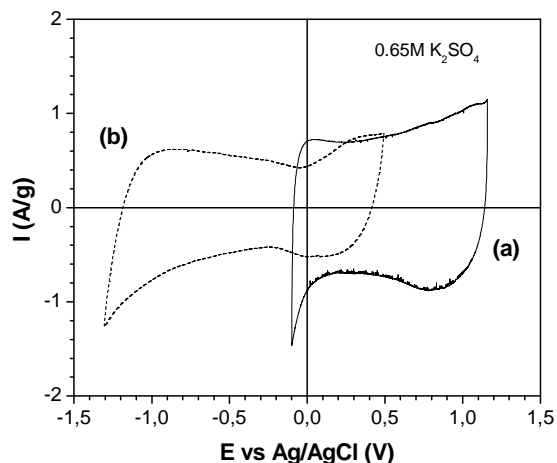


Figure 1. Cyclic voltammogram of: a) MnO₂ and b) activated carbon electrodes in a 0.65 M K₂SO₄ pH 6.5 solution.

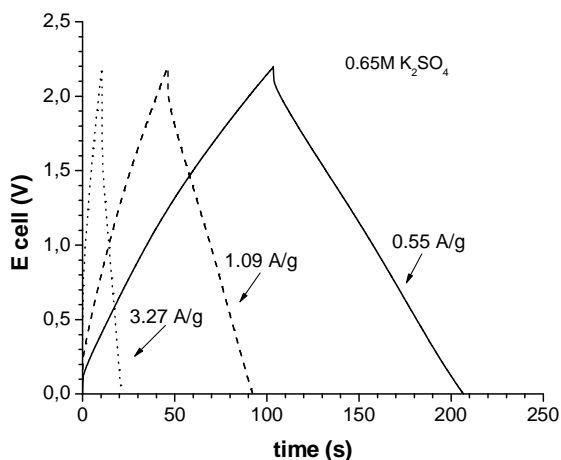


Figure 2. Constant charge/discharge curves for an activated carbon/MnO₂ capacitor.

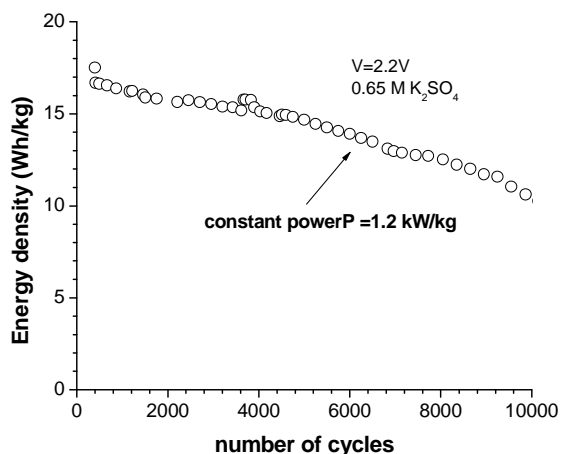


Figure 3. Variation of the energy density with the number of constant charge/discharge cycle.

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