

Coal tar pitch derived carbons for asymmetric electrochemical capacitors

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Introduction

High surface area coal tar pitch derived carbons with narrow pore size distribution (mean pore size ~ 0.8 nm) were synthesized and used as electrode materials for both aqueous symmetric and asymmetric electrochemical capacitors. Asymmetric capacitors were fabricated using pitch carbon/manganese dioxide with energy densities of 13 Wh/kg and a cell voltage of 2.0V. The asymmetric design takes advantage of strong electroadsorption of protons on microporous carbon aiding in improving the cell voltage [1-5]. We see further increase in cell voltage performance by synthesizing boron nitrogen containing carbons from polyborazylene/pitch precursors. The fabricated asymmetric capacitors using boron nitrogen carbons had an energy density of 22 Wh/kg and were cyclable for more than 300 cycles with an operable cell voltage of 2.5V, which is significantly high for aqueous electrolytes. The capacitor showed almost four times improvement in energy densities as compared to symmetric capacitors fabricated using coal tar pitch derived carbons.

Experimental

Coal tar pitch was dissolved in tetrahydrofuran and the soluble (THFS) and insoluble fractions (THFI) of the pitch were extracted. THFS was mixed with sulfuric acid (1:1 by wt.) and allowed to polymerize for 24 hours. The resultant viscous solution was pyrolyzed at 800 C for 1 hour under argon atmosphere. The sample was then activated using CO₂ to increase the surface area [1,2]. The sample was used for both the synthesis of symmetric as well as asymmetric coin cell capacitors.

0.5g of potassium permanganate was mixed with 10 ml of water (solution I). 0.05g of TritonX-100 was added to 20 ml of Hexane and 5 ml of methanol (Solution II). The two solutions were mixed together and let it stir for 10 minutes. The resultant mixture was then ultrasonicated for 5 minutes. The solution turned brown in color indicating the formation of Manganese dioxide. The solution was then filtered, washed and dried at 100 C to constant weight.

Coal tar pitch was dissolved in tetrahydrofuran (THF) and the soluble fraction of the pitch was extracted. The soluble fraction was mixed with polyborazylene and dissolved in THF. This was followed by co-precipitation in pentane. The

precipitate was then pyrolyzed under argon atmosphere to various temperatures.

For the activated carbon electrodes, a mixture 85 wt% carbon, 10 wt% Teflon and 5 wt% acetylene black was used. The manganese dioxide was a more resistive material, so more acetylene black was used for a mixture of 70 wt% manganese dioxide, 5 wt% Teflon and 25 wt% acetylene black. After the materials are mixed, THF was added to the mixture until a consistency of thin paint was achieved. This mixture was ultrasonicated for 30 minutes to insure even particle distribution throughout the THF. Once the ultrasonication was completed, the material painted onto a stainless steel or carbon mesh current collector with an ordinary paint brush and the THF is dried off using a heat gun set to a moderate temperature. After the THF is dried off, the electrode is ready to be used. The samples were used as electrodes painted on a tantalum foil in aqueous electrolytes for 3-electrode measurements.

A two electrode cell was constructed by using the synthesized electrode materials. A symmetric capacitor using pitch derived carbon electrodes, an asymmetric capacitor with pitch derived carbon/MnO₂ electrodes and boron nitrogen carbon derived from MnO₂ were made. The cell to be tested was hooked up to a 5210 amplifier and 263A potentiostat. This setup was used to perform the following tests: electrochemical impedance spectroscopy (EIS) tests, cyclic voltometry (CV) tests, and constant current (CC) tests on the electrochemical cells.

Results and Discussion

The electrochemical property of Manganese dioxide was studied using four different electrolytes in a scan range of 0 to 1 V vs Ag/AgCl. It was shown that the specific capacitance of the electrode was dependent on the nature of the cations and was the highest, when we used Magnesium chloride as the electrolyte (Mg>Ca>Ba>K). There also seems to be an optimum pH at which the specific capacitance of Manganese dioxide is maximum. The specific capacitance was the highest when the pH of Magnesium chloride was adjusted to 5 or 6 (Figure 8) and was close to 400 F/g. Similarly, the electrochemical performance of pitch derived carbon was tested in a scan range of 0 to -1V vs Ag/AgCl using KCl as electrolyte. Capacitance as high as 100 F/g can be obtained from this phenomenon and the strong electroadsorption of proton shifts the hydrogen evolution potential to almost - 1.0 V vs Ag/AgCl. The electroadsorption behavior of the carbon can be further enhanced when carbon derived from polyborazylene/pitch is used as a negative electrode. The protons do not desorb almost until 1.4 V vs Ag/AgCl. The result was highly surprising and encouraging as the N₂ BET surface area of the electroactive material was only 50 m²/g.

An electrochemical capacitor is essentially two capacitors in series, where each electrode and ion layer pair acts as a capacitor. In an asymmetric design, the mechanisms of charge

storage in the positive and negative electrodes are different. Hence, electrochemical parameter such as specific capacitance and reversible charge/discharge potential range for the electrodes can also be different. In order to optimize the performance of both the electrodes, it is required to balance the charges on both the positive and negative electrodes. Using the values of specific capacitance and pseudocapacitance potential ranges determined by 3-electrode measurements, it is possible to estimate the mass ratio of both electrodes needed to balance the charges as shown below:

$$q_+ = q_- \Rightarrow m_+ C_+ \Delta E_+ = m_- C_- \Delta E_-$$

$$\frac{m_+}{m_-} = \frac{C_- \Delta E_-}{C_+ \Delta E_+}$$

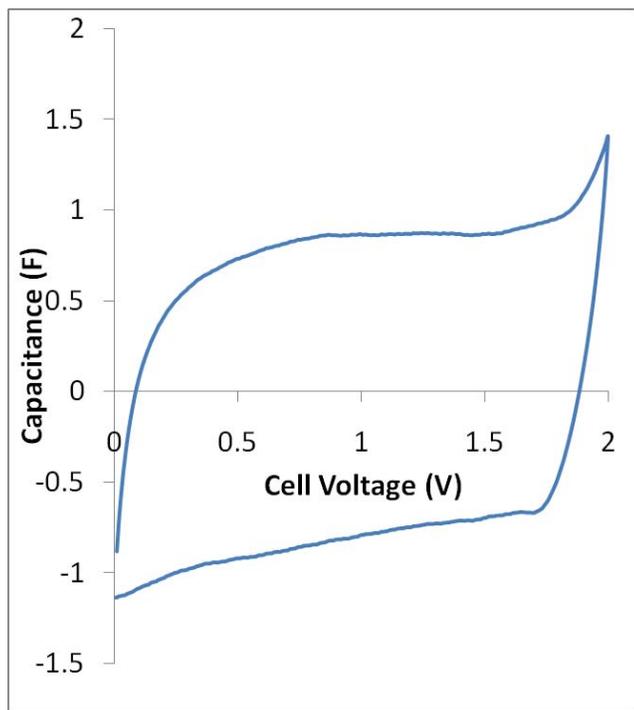


Figure 1. Cyclic voltammogram of activated carbon derived from pitch/manganese dioxide asymmetric capacitors in 2M aqueous magnesium chloride electrolyte

Asymmetric capacitor derived from pitch derived carbon/MnO₂ was constructed and a two electrode capacitor capable of operating at 2V in aqueous MgCl₂ solution was demonstrated as shown in Figure 1. The cell capacitance was about 0.8 F and the capacitor was cycled for 1000 cycles using galvanostatic charge/discharge method.

Asymmetric capacitor fabricated using polyborazylene /pitch blends has a cell capacitance of 0.6 F and cell voltage of 2.5 V (Figure 13), as high as organic electrolyte based capacitors. It was shown that energy densities as high as 22 Wh/kg can be obtained for this sample and there is very little capacitance fading even after 300 cycles. The results looked very

promising as we saw the energy densities improve by a factor of 4.

Conclusions

Asymmetric capacitors were fabricated using pitch derived carbons and manganese dioxide with energy densities as high as 22 Wh/kg. The cell voltage of the fabricated capacitors was extended upto 2.5V, as high as organic based electrolyte capacitors. However, since the designed capacitors are aqueous based electrolytes, the power densities are significantly higher than the organic electrolyte systems. The capacitors synthesized using boron nitrogen carbons were cyclable upto 300 cycles and further study is warranted to predict the cycle life.

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