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Methods for Manufacturing Carbon Electrodes for Supercapacitors: Pros and Cons

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As pure "physical" devices, which do not involve any chemical or electrochemical transformations, any charge or mass transfer across the electrode-electrolyte interface, SC's must demonstrate much faster charge/discharge operations and longer cycle life than any "chemical" batteries. Given this, SC devices can provide the key to a number of efficient power solutions that are mainly related with various backup systems to compensate short-term voltage surges or drops or with load leveling the batteries in various combined power sources. Low internal resistance can be one of key advantages of SC's over all other types of energy storage devices.

Keywords: Supercapacitor, Carbon electrode, Binder, Water-based, Manufacturing method.

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1. INTRODUCTION

Activated carbon is an excellent active electrode material for electrochemical double layer capacitors (EDLCs). It has the tremendous specific active area, usually greater than 1500 m2/g. It is non-toxic, electrically conductive and its structure can be tailored to specific applications. In organic electrolytes a working voltage of up to 3 volts per cell can be achieved. However, activated carbon is not easily converted into useful electrodes. A high-performance electrode must have:

- low electronic resistance;
- good electrolyte accessibility and wettability;
- a low contact resistance, stable interface with the current collector;
- high capacitance density (F/cm3);
- chemical stability;
- low level of electrochemically-active impurities;
- mechanical stability.

So, the particles of carbon powder must be held together in a compact manner to provide a low-resistance, high-density electrode [1]. This necessitates the use of a polymeric binder, which can maintain particle-to-particle contact, give the electrode mechanical integrity, and provide stable, low-resistance bonding to a current collector. The binder must be inert to the electrolyte, be stable at the electrochemical potential of the electrodes, be effective at low concentrations, and must not coat more than a small fraction of the activated carbon surface. A list of binders that meet these requirements and demonstrate good chemical and electrochemical stability include polytetrafluoroethylene (PTFE), polyvinylidenedifluoride (PVdF), polyvinyl alcohol (PVA), sodium carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR).

PTFE is a flexible polymer in a wide temperature range from -70 to +270 °C, but it has not any adhesion to aluminum current collector. Thus it needs a conductive layer to provide controlled adhesion and good electrical properties.

PVdF is known as a traditional binder that requires the use of volatile organic solvents, e.g., N-methyl pyrrolidone in its application. It is a semi-crystalline fluoropolymer that offers exceptional performance due to excellent coherence within electrodes and proper swelling properties with good mechanical strength. As a binder in electrode formulations, PVdF interconnects active materials to each other and to the conductive material (e.g. graphite, carbon black) to form the electrode material [2]. Stronger adhesion and cohesion results in stronger interfaces and, thus, in better performance.

Recently, sodium salt of carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) have been introduced as a suitable replacement in the manufacture of carbon electrodes for supercapacitors [3]. SBR/CMC composite agent is generally used in an aqueous binder: SBR as a primary binder and CMC as a thickening/setting agent. Adoption of the water soluble binder system definitely leads to cheaper and greener electrode processing [4].

The primary advantages of the water-based binder composition are as follows:

- use of a water solvent – environmental friendliness, process cleanliness and pollution-free;
- no need of environment control in the preparation – low facility requirements, thus reducing the cost of plant and equipment;
- fast drying speed and lower drying temperature, thus substantially decreasing the electric power consumption needs and speeding up the electrode production rate by ~ 1.5 times;
- no detectable difference in the electrochemical property as compared to the PVdF binder.

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2. EXPERIMENTAL

Four methods were chosen for further studying and manufacturing carbon electrodes, which were then tested in SC devices. These methods were: rolling, coating, screen-printing and spray technology. As active carbon electrode material the YP-80F (Kuraray Chemical Co., Ltd.) was chosen. Also the carbon black as a conductive additive was added. Active carbon layer was applied onto the aluminum current collector, which was coated with a conductive layer. 15 cm2 electrodes were assembled into SC cells (by 3 cells in each series) with organic electrolyte based on acetonitrile as a solvent (acetonitrile-based electrolytes accompanied with a special electrode design are mostly employed in YUNASKO technology) [5]. The key testing results were thoroughly verified and can be presented as in Table 1.

Table 1 – Physical and electrochemical characteristics of carbon electrodes in SC devices

Method	Thickness, μm	Density, g/cc	Specific capacity, F/cc	Specific resistance, Ω·sq.cm	Binder composition
Rolling	50	0.55	15.1	0.74	PTFE
Coating	60	0.48	14.6	0.71	PVdF
Screen-printing	35	0.45	10.1	0.92	PVA
Spray	45	0.47	10.2	0.82	CMC+SBR

*all electrodes were tested in SC cells in the YUNASKO laboratory

3. CONCLUSION

As can be seen from this Table, all YUNASKO carbon/carbon devices demonstrate very low inner resistance (hence, very fast charge and discharge are possible) along with a high capacitance. The best result demonstrate those devices, which are comprised the rolling electrodes due to their network of fibrils instead of a polymer film. But it is a difficult scalable method.

Cost, environment, safety concerns lead to switch from non-aqueous to aqueous processing techniques, thus coating as an electrode manufacturing method will be very promising with the use of water-based binder composition such as CMC and SBR

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