EFFECT OF METAL LOADING ON THE PERFORMANCE OF ACTIVE CARBON AS THE ELECTRODE MATERIALS OF EDLC

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Abstract:

Both some metal oxide and porous carbon materials can be used as the electrode materials of EDLC, but neither will have satisfied commercial application because of high cost, source shortage or low capacitance. Some cheaper transition metals which have pseudocapacitance such as Mn, Co, Ni, Fe, Y, Mo, Cu were loaded to the surface of AC for trying to improve the capacitance of EDLC. The results indicated that compared with original AC, AC with Cu, Mn, Co, Ni loading showed higher capacitance, while AC with Fe, Y, Mo loading exhibited relatively lower capacitance. It is very interest that AC with Cu loading had extremely high capacitance although the capacitance markedly decreases with the increase of cycle number, even after 15 cycle it still had much higher capacitance than AC without metal loading.

Key words: Metal loading, active carbon, EDLC

Introduction

EDLC is becoming growing demands in the devices such as electric vehicles that require high power density and energy density in a short pulse. The electrode materials strongly affect the performance of EDLC. At present, there are three sorts of electrode materials-metal oxide, conducting polymer and porous carbon. The former two materials store the charge by the redox pseudocapacitance mechanism, they have high specific capacitance (for example, 220F/g for conducting polymer and 840F/g for metal oxide [1-3]), but their commercial application in a large scale is restricted because of high cost and source shortage. In contrast, the porous carbon materials make use of electrochemical double-layer for storing charge, so they have fast rate of charge and discharge but lower capacitance (180F/g [4-6]), even so, they are still widely used in the commerce because of lower cost and more sources.

Because single material showed limited performance, the composite which may have the advantage of each material was suggested for improving the capacitance of EDLC [7-11]. For example, the capacitance of carbon aerogels with ruthenium deposition or carbon nanotube-conducting polymer composite was higher than pure single material. However, Ru is a expensive rare metal and conducting polymers is not easily available, so some transition metals with pseudocapacitance such as Mn, Co and Ni maybe a

alternative way [7].

In this work, the composites of cheaper transition metal (Mn, Co, Cu, Fe, Mo, Y and Ni)-active carbon were prepared, and the effect of metal on the capacitance of AC as electrode materials of EDLC was investigated.

Experimental

Pitch-based AC was prepared via traditional method using steam as activating agent. Its specific surface area, pore volume and average pore diameter is 761 m^2/g, 0.46cm^3/g and 2.42nm, respectively.

1g AC was immersed into the solution of 1wt% metal nitrate of 100ml at room temperature for 24h, then filtered and fried overnight at 120℃. The dried powder was decomposed under N_2 at 500℃ for 2h to produce the composite of AC and metal oxide. The similar procedure was used as the preparation of ACs with different copper contents, just changing the concentration of $Cu(NO_3)_2$ into 0.5, 1 and 2wt% respectively.

The electrode of EDLC was fabricated as a thin, circular sheet type (weight of AC composite: 20-30mg) with surface area of 1 cm^2, using 78wt% AC composite, 20wt% graphite, and 2wt% PTFE.

The capacitor was composed of AC sheets which were sandwiched by a separator and 30wt% KOH electrolyte.

The electrochemical measurements were carried out by BT4+ model battery instrument which produced by American Arbin Instruments , the software for processing data is MITS"97. The current of charge and discharge is 1mA. The obtained specific capacitance was calculated by single electrode.

Results and Discussion

Fig. 1 illustrated the sorts of metal loading are how to affect the capacitance of AC. Compared with original AC, ACs with Mn, Co, Ni loading showed higher capacitance, while ACs loaded by Y, Fe, Mo are of relatively lower capacitance. At the first several cycle, the capacitance of all the AC electrodes decreased gradually except the Cu-AC electrode, afterwards becoming basically constant. This phenomenon may be explained that part of metal species which adsorbed weakly on the surface of AC dissolved into the KOH electrolyte, resulting in the decrease of capacitance at the beginning of electrochemical process. With the gradual dissolution of weakly adsorbed metal species, the relatively strongly attached metal species on AC were left for contributing the steadiness of capacitance.

It is very worthy to note that AC with Cu loading showed extremely large capacitance although its capacitance remarkably decreased with the increase of cycle number. The similar phenomenon was observed by Shu-Rong Hwang and Hsisheng Teng [12], They suggest the capacitance enhancement may partially result from the reversible redox transitions of Cu in the presence of OH⁻ ions, and the formation of surface complexes that

serve as centers for reversible redox reactions may be responsible for the capacitance increase.

The reason of the rapid capacitance decrease in Cu-AC electrode during cycle may be the solubility of copper hydroxide , which was formed through the reaction of copper species and KOH, is much larger than one of Mn, Co, and Ni hydroxide, so easily dissolving into the solution of electrolyte to lead to the rapid decrease of copper species on the AC, therefore the distinctly instable capacitance.

Fig. 1 Discharge capacitances of the different AC-metal composite electrodes

The amount of Cu loading also observably influenced the capacitance of AC and the stability of EDLC (Fig. 2). AC-Cu-2 exhibited the capacitance of 1.15mAh at the first cycle, and still was high more than 0.63mAh even after 15th cycle, being the highest capacitance among three different metal loading amounts, however its instability was also remarkable. When the loading amount was decreased into 1wt% (AC-Cu-1), the capacitance accordingly decreased, but its capacitance stability became improvement. The further decreasing loading amount led to almost constant capacitance (AC-Cu-0.5), its capacitance decreased only 13% from the first cycle to the 20th cycle. Even so, 0.53mAh at the 20th cycle was still higher than 0.37mAh of original AC.

Fig. 2 Discharge capacitances of the EDLC with different electrodes

Fig. 3 showed the charge-discharge curve of AC with Cu loading (AC-Cu-1). It can be seen that the normal linearity relationship between the voltage and the time of charge-discharge was changed into a curve because of the Cu loading on AC. There is a discharge voltage platform around 0.1V, indicating that the charge in Cu species was chiefly desorpted through redox reaction around 0.1V, and the discharge time of the platform was gradually short with the increase of cycle number (Fig. 4).

Fig. 3 Charge-discharge curve of Cu-AC the electrode

Fig. 4 Charge-discharge curves of the electrode doping with Cu

Conclusion

Some transition metals which have pseudocapacitance such as Cu, Mn, Co, Ni can be used for improving the capacitance of AC electrode in EDLC, especially AC with Cu loading show extremely high capacitance, but its cycle performance is poor because of the high solubility of Cu species in KOH electrolyte. To solve this problem, one can use organic electrolyte instead of aqueous solution, alternatively, change the preparation method of AC-metal composite, for example, doping metal species to some polymer, then carbonizing and activating the obtained mixture for preparing AC which metal species are uniformly dispersed inside AC. The latter method is under progress.

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