

Electrochemical Characteristics of Pseudocapacitor Using Aqueous Polymeric Gel Electrolyte

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Abstract. We have reported to make nanostructured cobalt oxide electrode that have large capacitance over than 400 F/g (specific capacitance) and good cycleability. But, it had serious demerits of low voltage range under 0.5 V and low power density. Therefore, we need to increase voltage range of cobalt oxide electrode. We report here on the electrochemical properties of sol-gel-derived nanoparticulate cobalt xerogel in 1 M KOH solution and aqueous polymeric gel electrolyte. In solution electrolyte, cobalt oxide electrode had over 250 F/g capacitance consisted of EDLC and pseudocapacitance. In gel electrolyte, cobalt oxide electrode had around 100 F/g capacitance. This capacitance was only electric double layer capacitance of active surface area. In solution electrolyte, potassium ion as working ion reacted with both of layers easily. However, In gel electrolyte, reacted with only surface-active layer. It's very hard to reach resistive layer. So, we have studied on pretreatment of electrode to contain working ions easily. We'll report more details.

Key words: Supercapacitor, Hydro gel, Polymer electrolyte, Cobalt oxide

1. Introduction

Electrochemical capacitors (supercapacitors) are being increasingly discussed not only for backup power which is an established application to electronic equipments and computers^{1,2)}, but also for high power applications in pulsed lasers and electric vehicles^{3,4)}. In the latter cases, it is envisaged that supercapacitors will provide bursts of power during acceleration and will be used in conjunction with high energy density lithium batteries. We previously reported pseudocapacitors containing aqueous solutions systems, nanostructured cobalt oxide as an active material for an electrode, 1 M KOH solution as an electrolyte⁵⁾. The nanostructured cobalt oxide electrode had a large capacitance over than 400 F/g (specific capacitance) and good cyclability. However, it showed low working voltage range under 0.5 V and a low power density as serious demerits. Therefore, we needed to increase the voltage range of the cobalt oxide electrode.

The applications of polymeric electrolytes to supercapacitors can lead to thin film cells and high reliability without leakage of liquid components. Generally, polyethylene oxide (PEO) lithium perchlorate solid-polymer electrolytes have a high internal-resistance at ambient temperatures, which makes them unattractive for several applications. Gel electrolytes based on a combination of PEO, polymethylmethacrylate (PMMA) and propylene carbonate (PC) with lithium perchlorate salt have been reported by Ishikawa *et al.*⁶⁾. These gels are superior to solid polymer-electrolytes based on PEO, which contains lithium salts, in terms of their conductivity, and they also possess adequate mechanical

strength. Ishikawa *et al.*⁷⁾ have also examined the use of polymer-gel electrolytes based on polyacrylonitrile (PAN) and PC for capacitor applications. These polymeric electrolytes, however, were investigated for EDL capacitors. There has been no study in an attempt to use gel electrolytes for pseudocapacitors. Polyacrylic acid (PAA) hydrogels have been used extensively in medicine and pharmacy as drug delivery systems, contact lens, catheters, wound dressings, and biosensors^{8,9)}. It showed excellent swelling behaviors in aqueous solution.

In this work, therefore, we tried to develop a new type gel electrolyte for pseudocapacitors using an aqueous polymeric gel electrolyte with PAA hydrogels.

2. Experimental

2.1. Preparation of electrode & electrolyte

Nanostructured cobalt oxide was used as an active material for our electrode according to our previous work⁵⁾. The electrode consisted of 75 wt.% cobalt oxide powder, 20 wt.% acetylene black as conducting material and 5 wt.% PTFE as a binder.

Electrode was prepared using 5 mm Φ punch and then placed on Ni gauze (Nilaco Co.) as a current collector.

PAA (Aldrich Chemicals) gel was prepared by adding 0.5 g of PAA to preheated 10 ml of 1 M KOH solution at 85°C.

2.2. Electrochemical measurements

Electrolytic conductivity was determined by an ac. impedance measurement system. In this measurement, a screw type cell was used. The gel was sandwiched by stainless electrodes in the cell. A good contact between gel and electrodes was obtained with springs that pressed the electrodes against the

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gel. A thickness of the gel film was c.a. 1.2-1.3 mm.

Stable potential windows were determined by potential sweep voltammetry. The measurement was carried out using a potentiostat(Nikko Keisoku, NPGS-301) and a function generator(Hokuto Denko, HB-107A). Platinum plates were used as a working electrode and a counter electrode. Silver wire was selected as a reference electrode. The capacitor performance was investigated by repeat of charge-discharge.

3. Results and Discussion

3.1. Capacitance change of cobalt oxide electrode with the electrode content

In order to determine a good composition ratio of cobalt oxide electrode, the capacitance with different ratios of active material(cobalt oxide) to conducting material(acetylene black) and binder(PTFE) content were measured in 1 M KOH solution(Fig. 1).

With increasing of conducting material content ratio, the capacitance was increased on account of improvement in cobalt oxide inner resistance. When conducting material amount was poor, double layer capacitance was only shown without pseudocapacitance. On the contrary, not only double layer capacitance but also pseudocapacitance was shown in higher conducting material content ratio, judging from the presence of pseudo-plateau in the discharge curve. Furthermore, it kept the higher capacity than the electrode with AB 10% as shown in Fig. 2. Therefore, in this work, electrochemical measurements were carried out based on cobalt oxide 75 wt%, acetylene black 20 wt%, PTFE 5 wt%.

3.2. Electrochemical behavior comparison between aqueous solution and aqueous polymeric gel

We compared electrochemical behavior of cobalt oxide electrode in aqueous solution with that in gel electrolyte(Fig. 3). While the cobalt oxide electrode in aqueous solution can utilize both surface EDLC and internal pseudocapacitance on account of facile intercalation of K^+ ion as a charge carrier to the electrode, the behavior in aqueous polymeric gel electrolyte

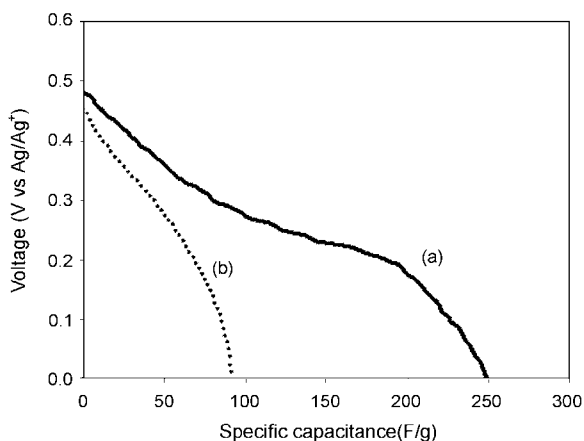


Fig. 1. Specific capacitance of the electrodes with different content ratio; (a) Co 75%, AB 20%, PTFE 5%, (b) Co 80%, AB 10%, PTFE 10%.

implies utilization of only surface EDLC. Nevertheless, working voltage was increased from 0.4 V to 0.8 V.

As shown in Fig. 4, capacitance decreased in the aqueous solution electrolyte with increasing cycle numbers.

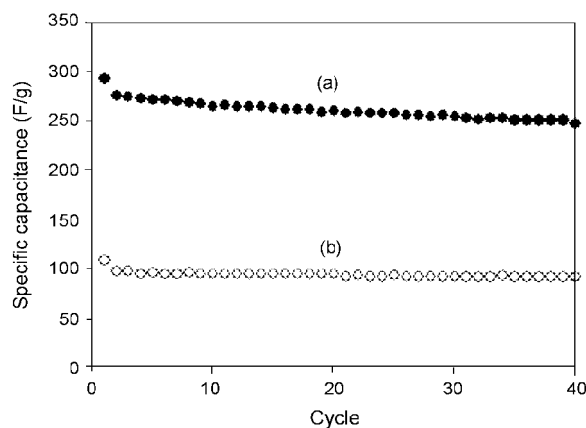


Fig. 2. Cyclability of electrodes with different content ratio; (a) Co 75%, AB 20%, PTFE 5%, (b) Co 80%, AB 10%, PTFE 10%.

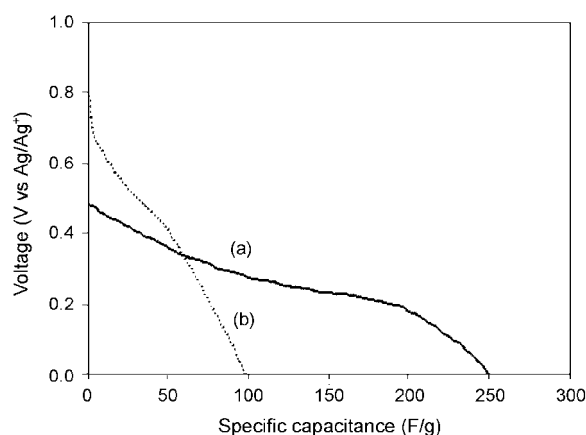


Fig. 3. Specific capacitances of electrodes with Co 75%, AB 20%, PTFE 5% composition; (a) 1 M KOH solution, (b) 1 M KOH gel.

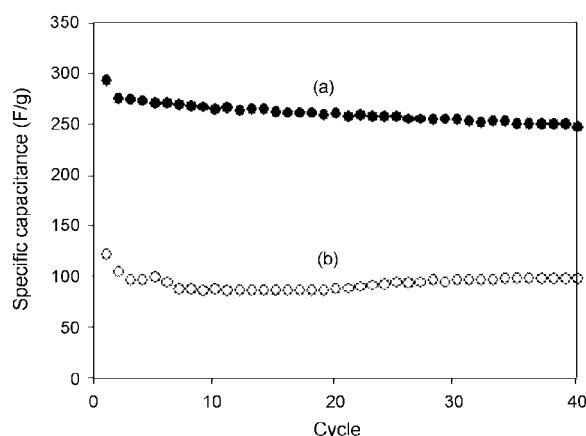


Fig. 4. Cyclability of electrodes with Co 75%, AB 20%, PTFE 5% composition; (a) 1 M KOH solution, (b) 1 M KOH gel.

On the contrary, capacitance increased in the aqueous gel electrolyte. The reason why capacitance increased in the gel electrolyte is that more enough cycles would be necessary to intercalate working ion, K^+ , into the electrode.

Therefore, pretreatment of electrode was needed for the purpose of making a working ion intercalate easily into the electrode.

3.3. Capacitance changes of cobalt oxide by various pretreatments

Figure 5 shows capacitance changes with some pretreatment of the cobalt oxide electrode in order to enhance the ion intercalation into the inner electrode.

We used potential scan(PS) method and constant voltage method in the aqueous solution electrolyte. PS method was performed between 0.0 V and 0.8 V in 1 M KOH solution as an electrolyte, and Ag/AgCl electrode was used as a reference electrode. The scan rate was 1 mV/s. With comparing the performance after 1 cycle PS with that after 10 cycles PS, capacitances were found to be almost same. Therefore, 1 cycle PS pretreatment was enough for the activation. Furthermore, looking at fast charge/discharge properties, it showed good performance at both 2.5 mA and 8 mA charge/discharge rates.

Constant voltage method was measured at 0.8 V for 1 hour. That should make an oxidation layer on cobalt oxide electrode surface and increase the surface area. Compared with the PS method, capacitance after the potential application was high at 2.5 mA/cm² rate especially by increasing cycle number. However, it could not be distinguishable from the result with PS method at 8 mA/cm² rate.

Figure 6 shows the capacitance changes of IPS pretreatment electrode with cycle numbers. After the pretreatment and initial 80 cycles (Fig. 5), subsequent cycling was carried out over 100 cycle to confirm the electrode stability. The coulomb efficiency was more than 95% and capacitance increased slowly by increasing cycle numbers.

4. Conclusion

We developed new aqueous polymeric gel electrolyte in order to increase working voltage of cobalt oxide electrode. Polymeric electrolytes for pseudocapacitors have never been studied so far. When the cobalt oxide electrode was used in aqueous polymeric gel electrolyte, working voltage increased from 0.4 V to 0.8 V thus power density was increased. In pretreatment test, PS method was better than constant voltage method. This work was the first attempt to use a gel electrolyte for pseudocapacitors. Though the gel system shows lower capacitance compared to that in the aqueous system, has possibilities of gel electrolyte for pseudocapacitor applications.

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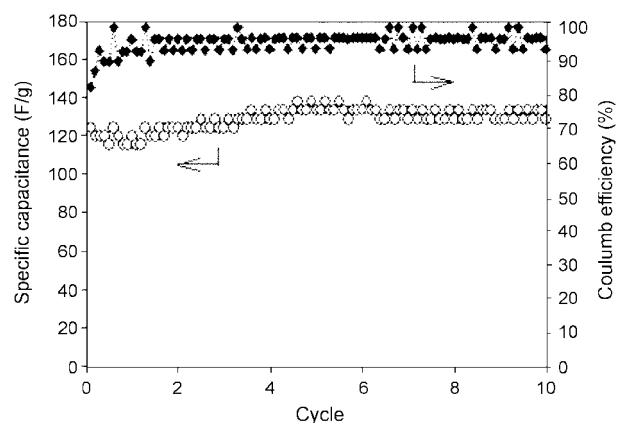


Fig. 5. Capacitance changes of electrode with Co 75%, AB 20%, PTFE 5% composition with different pretreatment.

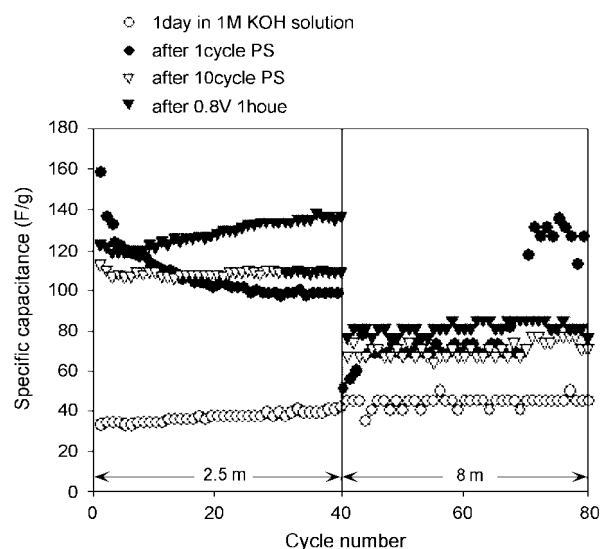


Fig. 6. Capacitance changes and coulomb efficiency as a function of cycle numbers.

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