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Short Communication

Graphite nanosheets as an electrode material for electrochemical double layer capacitors

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ABSTRACT

In this paper, the effect of ion sizes of cations and anions on the charge storage capability of graphite nanosheets is investigated. Electrochemical properties of prepared electrodes are studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques, in 3 M NaCl, NaOH and KOH electrolytes. A scanning electron microscope (SEM) is used to characterize the microstructure and nature of prepared electrodes. SEM images and XRD patterns confirm the layered structure (12 nm thickness) of the used graphite with an interlayer distance of 3.36 Å. The electrochemical results and the ratio of q^*_O/q^*_T confirm a better charge storage and charge delivering capability of prepared electrodes in 3 M NaCl electrolyte. The charge/discharge cycling test shows a good reversibility and confirms that the solution resistance will increase after 500 cycles.

1. Introduction

Recently, electrochemical capacitors have attracted worldwide research interest. Depending on charge storage mechanisms, capacitors can be classified into three types: electrochemical double layer capacitors (EDLCs), faradaic pseudocapacitors and hybrid capacitors [1,2]. Especially in EDLCs and at high charge/discharge rates, since no chemical reaction is involved, the effects are easily reversible with minimal degradation in deep discharge or overcharge and the typical life cycle is hundreds of thousands of cycles [3,4]. With respect to the electrode materials there are three main categories: carbon based materials, transition metal oxides and conductive polymers [5,6]. Among carbon based materials—due to good conductivity, superior chemical stability, large surface area-to-volume ratio and unique layered structure—graphite has competed with carbon nanotubes, activated carbon, etc. which are used as electrode material for ECs. High surface area of graphite does not depend on the distribution of pores in solid state, but comes from the interconnected open channels between graphite layers distributed in a two-dimensional architecture [7–9]. However, the major problem of such a material is that not all the BET surface area is electrochemically accessible [10]. Ion sizes in electrolyte and the charge/discharge rate are significant parameters affecting the ratio accessible to the total surface, energy storage and power capability of graphite electrodes. Therefore, choosing a proper electrolyte in accordance with the morphology may be effective.

In this paper, the effect of ion size on charge storage, charge delivering capability and reversibility of graphite electrodes was investigated using cyclic voltammetry and electrochemical impedance spectroscopy techniques. The morphology and nature of the prepared electrodes were investigated employing a scanning electron microscope.

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2. Experimental

2.1. Materials

Graphite nanopowder (12 nm Flakes, multi-layered) with the specific surface area of 15 m^2/g and purity of 98.5% was purchased from graphite supermarket and polytetrafluoroethylene (<2 μm) from Aldrich company. All other chemicals used in this study were purchased from Merck. 90 wt% graphite nanopowder and 10 wt% polytetrafluoroethylene (PTFE) were well mixed by ultrasonic wave in ethanol in paste form for about 60 min. Paste form was chosen for better dispersion of PTFE in graphite nanoflakes. After drying the paste and powdering, the composite was pressed onto a 316L stainless steel plate (5×10^7 Pa) which served as a current collector (surface area was 1.22 cm^2). A steel rod and a hollow cylinder of epoxy were used for pressing. The composite is pressed onto the epoxy properly by the steel rod. A Teflon paper was used at the bottom of the rod because of its very low adhesion, in order to stick the composite material to the stainless steel substrate. The typical mass load of the electrode material was 45 mg. The electrolytes investigated were 3 M NaCl, NaOH and KOH.

3. Characterization

Electrochemical behavior of prepared electrodes was characterized using CV and EIS tests. Electrochemical measurements were performed using an Autolab (Netherlands) Model PGSTAT302N. CV tests were performed within the range of -0.55 and $+0.3$ V (vs. SCE). EIS measurements were carried out in the frequency range of 100 kHz–0.02 Hz at OCP with an AC amplitude of 10 mV. The specific capacitance C (F g^{-1}) of the active material was determined by integrating either the oxidative part or the reductive part of the cyclic voltammogram curve ($Q(C)$). This charge was subsequently divided by the mass of the active material m (g) and the width of the potential window of cyclic voltammogram ΔE (V), i.e.,$C=Q/(m\Delta V)$ [11–13].

4. Results and discussion

Ion size and diffusion of anions and cations are effective parameters of specific capacitance. When the KCl and NaCl electrolytes are compared, the pronounced difference is of cation nature. Ionic radii of K^+ and Na^+ are 146 and 135 pm, respectively. In water solutions hydroxide ions are bigger than protons (ionic radius of H^+ and OH^- is 35 and 153 pm, respectively) which may lead to hindrance in the diffusion of potassium or sodium ions and lead to non-capacitive behavior. On the other hand, ionic mobility of K^+ is larger than Na^+ but ionic radius is smaller. However, electrochemical nature of KCl electrolyte is close to that of NaCl electrolyte. In addition to the ionic characteristics, nature of the active material is an effective parameter of capacitance. The SSA (specific surface area) of graphite used in this paper is about 15 m^2/g but graphene (in all forms) almost shows a higher SSA. The higher SSA of graphene than that of graphite is the main reason for increasing the capacitance (Table 1). Additionally, CB is characterized by high porosity and small particle size. These porosities are also varied from mild surface pitting to the actual hollowing out of particles. The surface area of CB is considered to be more accessible generally than the other forms of high surface area carbons; this fine highly branched structure of CB particles makes them ideally suitable for filling inter-particle voids created between coarse particles which improves the electrical contact between them and increases the capacitance (Table 1).

Specific surface area and conductivity are two important parameters to prepare highly efficient electrodes for capacitors. But only a part of the surface is always accessible by electrolyte ions to be adsorbed. This would increase the solution resistance. Fig. 1(a) shows the SEM image of prepared electrodes, confirming the 2D graphite nanosheets consisting of several carbon atom layers with a total thickness of about 12 nm. Graphite layers interact with each other to form open pore systems through which ions easily access the surfaces between the graphite nanosheets to form an electric double layer. Distance between these nanosheets was measured using XRD and was about 3.36 Å (Fig. 1(b)). The graphite used was perpendicular to these nanosheets, showed no porosity and was completely flat (Fig. 1 (a)). Thus, the used material is in its 2D porous and 1D flat surfaces completely. With this morphology, it seems that the charge storage depends directly on the charge separation on flat part (which is the most accessible surface of electrode) and on open pore systems (which are less accessible and ion size dependant). Ion size and ion diffusion through these pores would affect the activation of these less accessible surfaces, especially at high scan rates [14]. Increasing the ionic radius would decrease the number of adsorbed ions on the unit surface area of the electrode. This would decrease the charge stored on the outer Helmholtz layer. Therefore, for further investigations 3 M electrolytes of KOH, NaOH and NaCl were employed. The main difference in these electrolytes is the effective radius of their anions and cations. Na^+, K^+, Cl^- and OH^- ions have effective radii of 102, 138, 181 and 153 pm, respectively. The ratio of interlayer distance of graphite 3.36 Å to ionic radius (α) for these ions would be 3.29, 2.43, 1.86 and 2.20, respectively.

The capacitance of each electrode was calculated from the *CV* curves using

$$C_s = \int i \, dV / ms\Delta V \tag{1}$$

where C_s is the specific capacitance, $\int i\,dV$ is the integrated area of the CV curve, m is the mass of the active material (mass of electrode material regardless of mass of PTFE), ΔV is the potential range, and s is the scan rate.

Table 1
Comparison of different carbon based materials in KCl electrolyte.

Active material	Electrolyte	Specific capacitance (F g^{-1})
Carbon black [22]	3 M KCl	33.58
Activated carbon [23]	1 M KCl	29
Multilayer graphene [24]	1 M KCl	15.6
Few layer graphene [24]	1 M KCl	14.9
Single layer graphene [24]	1 M KCl	10.9