Contribution of surface oxygen groups to the measured capacitance of porous carbon supercapacitors

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HIGHLIGHTS

- Porous carbon materials were treated at 950 °C for 3–18hr to remove oxygen groups.
- Heat treatment increases the porous carbon's SSA but does not alter its pore sizes.
- The contribution of oxygen groups to a carbon material's capacitance is quantified.
- Phenol & carboxyl groups are electrochemically active in alkaline KOH electrolyte.
- The phenol & carboxyl groups each contribute $1.10\,\mu F\,cm^{-2}\,at\%^{-1}$ in 4 M KOH electrolyte.

GRAPHICAL ABSTRACT
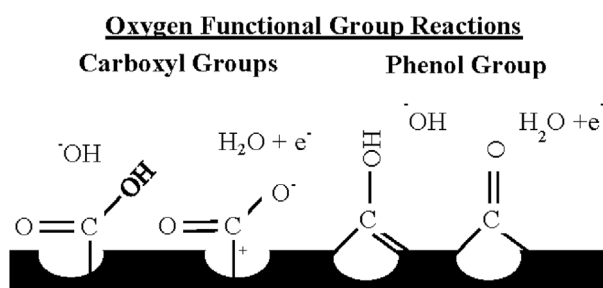
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ABSTRACT

Porous carbon is used as the electrode material in electrochemical double-layer capacitors (EDLCs) due to its high surface area and electrical conductivity. However, one of the challenges associated with porous carbon is the presence of electrochemically active surface oxygen groups, which undergo rapid charge transfer reactions in alkaline or acidic electrolytes. In this study, oxygen groups have been removed from porous carbon samples in order to quantify their contribution to the double-layer capacitance. The oxygen-free porous carbon samples have similar pore size distributions to the original sample; however, the specific surface area (SSA) is observed to increase slightly with heat treatment. The original porous carbon sample, containing oxygen, has an SSA-normalized capacitance of $12.2\,\pm\,0.2\,\mu F\,cm^{-2}$, while the oxygen-free samples have SSA-normalized capacitances of $8.8\,\pm\,1.0\,\mu F\,cm^{-2}$, regardless of total SSA. Based on these results, the relative contributions of the carboxyl and phenol oxygen groups are determined, which are the two electrochemically active oxygen groups in alkaline solutions. From this work, it is shown that the carboxyl groups and phenol groups contribute approximately $1.10\,\mu F\,cm^{-2}\,at.\%^{-1}$. These results demonstrate the importance of oxygen groups for accurate characterization of the performance of novel porous carbons for EDLCs.

1. Introduction

There is an ever-increasing need for efficient electrical energy storage devices for a wide array of applications, including portable electronics, electric vehicles, and grid power management. Due to the broad range of power and energy requirements, and charging cycles, several different electrical energy storage devices are required. The typical electrical energy storage devices are capacitors, batteries, and

supercapacitors.

Supercapacitors offer the benefits of high power density, high cyclability, and rapid charging rates. Supercapacitors are limited by their moderate energy density compared to batteries [1–8].

There are three types of supercapacitors, electrochemical double-layer capacitors (EDLCs), which store energy by ion adsorption on the electrode surface, pseudocapacitors, which store energy using electrochemically active materials that undergo rapid faradaic charge transfer reactions, and hybrid capacitors, which combine the advantages of EDLCs and pseudocapacitors [1–8]. The energy storage mechanism of EDLCs is based on physical adsorption of electrolyte ions on the surface of porous carbon electrodes. This forms the EDL, which acts as a capacitor. Therefore, in order to maximize capacitance, electrolyte accessible surface area, and pore size distribution must be controlled [1,7–15]. The typical capacitance for activated carbon based EDLCs ranges between 50 and 350 $F g^{-1}$ in aqueous electrolytes [6,10].

It was hypothesized by Xia et al. that the maximum achievable SSA-normalized capacitance for a single sheet of graphene was 21 $\mu F\,cm^{-2}$ [16]. This model calculation assumes that the electrolyte ions occupy the basal plane surface of the graphene sheet; however, does not account for ion adsorption on the edges of the graphene sheets. It was predicted by Kinoshita that the edge plane of graphene would have a higher maximum SSA-normalized capacitance, between 50 and 70 $\mu F\,cm^{-2}$ [17].

Activated carbon electrode EDLCs have yet to achieve these high theoretical SSA-normalized capacitance values, with the typical values for EDLCs with aqueous electrolytes between 8 and 11 $\mu F\,cm^{-2}$ [6,10]. In 3-D porous carbon materials there are several factors that affect the material's capacitance. In these porous carbon materials, with various pore sizes, the total surface area is not completely accessible. Additionally, there has been considerable debate relating to the effects of carbon structure and pore size pores on the capacitance of activated carbon materials. The initial theories demonstrated that the capacitance was enhanced by sub-nanometer pores, which are slightly smaller in diameter than the hydrated diameter of the electrolyte ions. It was hypothesized that in these sub-nanometer pores, the thickness of the EDL is reduced which leads to a greater theoretical capacitance [18–26].

However, there have been several studies countering this theory, demonstrating that mesopores (2–50 nm in diameter) result in higher capacitances [27–31]. Results from more recent studies have supported the initial theories, identifying that sub-nanometer enhance a carbon material's capacitance. The theory that has been supported is that in sub-nanometer pores, the EDL is thinner due to ion desolvation, resulting in ions penetrating and adsorbing in pores similar to their hydrated radius [32–37]. These studies demonstrate that the capacitance of a material can be greatly affected by its pore size distribution, and that this can play a key role in the material's performance. Therefore, in order to truly isolate the contribution of another property of the carbon material, such as oxygen content, it is clear that the pore size distribution of the materials must be controlled.

In recent scientific literature, there has been considerable interest in the relationship between capacitance of basal plane carbon and edge plane carbon. In these studies both experimental and mathematical models were used to investigate the effects of increasing the carbon edge sites. It was observed in all cases that capacitance was increased when there were more carbon edge sites [38–42]. It has also been suggested by Kim et al. that using potassium hydroxide (KOH) as the chemical activating agent leads to increased edge sites, since the KOH will fracture the graphitic structures [39].

Another factor that can affect the performance of porous carbon materials is the surface functional groups, primarily relating to oxygen functional groups [2,43–45]. There are four key oxygen functional groups, shown in Fig. 1.

Quinone groups and carbonyl groups are known to react with hydronium ions in acidic solutions, and carboxyl and phenol groups are known to react with hydroxide ions in alkaline solutions. The reactions between the carboxyl and phenol groups and hydroxide ions are displayed in Fig. 2 and Fig. 3, respectively [43–45]. In this study, alkaline electrolytes were used; therefore, the carboxyl and phenol reactions will be the primary focus.

In order to study oxygen functional groups, graphene oxide is typically reduced in order vary the amount of surface oxygen functional groups, and study their relative effects on the measured capacitance. It has been found that oxygen functionality tends to increase the capacitance of a material in both acidic and alkaline electrolytes [43–45]. The synergistic effects of oxygen and nitrogen have also been studied, by doping porous carbon with nitrogen and oxygen functional groups. It was found that oxygen and nitrogen functional groups tend to be found in larger pores, greater than 1 nm, and that in acidic electrolytes, quinone oxygen groups, and pyridinic and pyrrolic nitrogen groups had the most prominent effects on capacitance [46]. Similarly, Oh et al. found that in reduced graphene oxide materials, quinone oxygen groups had the greatest contribution to the capacitance, and the carboxyl and phenol oxygen groups have the least impact on the material's measured capacitance [43]. Therefore, surface oxygen functional groups play a critical role in the capacitance of porous carbon materials. However, in alkaline electrolytes oxygen functional groups have a lower contribution to the overall material capacitance.

It has also been found that oxygen rich porous carbon materials tend to have increased SSA normalized capacitance values [31,47,48]. However, there has been no clear consensus on the effects of oxygen in broad pore size distribution, porous carbon materials.

In this study, the effects of oxygen functional groups and total surface area are studied in order to determine their effects on capacitance. Heat treated porous carbon samples were prepared in order to remove the oxygen functional groups and adjust the surface area of the materials.

2. Experimental

2.1. Raw materials

Oil sands fluid petroleum coke (OSFC), supplied by the Canadian Oil Sands Industry was used as the raw material to prepare porous carbon samples, as presented in Zuliani et al. [49]. The OSFC material is a carbon dense (~80 wt%) free flowing powder of nearly spherical particles. The particle size of the OSFC used for porous carbon preparation was controlled to 150–212 μm. Potassium hydroxide, supplied by Sigma Aldrich, was used as received.

For the composite electrodes, carbon black (CB), supplied by Alfa Aesar, was used as supplied, as well as 60 wt% polytetrafluoroethylene (PTFE) suspension, from Sigma Aldrich, and was used as supplied. All solvents were used as supplied.

2.2. Porous carbon preparation

The porous carbon preparation was performed in two steps, first a chemical activation with potassium hydroxide, and second a long-term heat treatment.

The chemical activation of the OSFC was performed following a similar procedure to those cited in Refs. [37,49]. The 25 g of OSFC was mixed with potassium hydroxide in a mass ratio of 3.5:1 KOH:Coke, along with 0.3 g of methanol, and 5 mL of water. The mixture was allowed to stand at ambient conditions for 20 h. Chemical activation was performed in an inert nitrogen atmosphere. During the activation, the material was held at 400 °C for 2 h and 850 °C for 2 h, with a temperature ramping rate of 5 °C min^{-1}. After activation, the activated OSFC (AFC) was allowed to cool and was washed with distilled water and dilute hydrochloric acid to remove any residual alkaline activating agent.

After chemical activation, the AFC samples underwent long term