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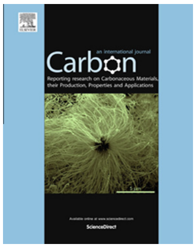

Wettability of colloid-imprinted carbons by contact angle kinetics and water vapor sorption measurements

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ABSTRACT

As an example of nanoporous carbon materials, colloid-imprinted carbons (CICs) have been reported to have promising properties for use in a variety of applications. However, the wettability of these carbons has not been investigated as yet. In this work, CICs with different pore sizes (20–50 nm) were synthesized and heat treated at 1500 °C under a N_2 atmosphere. Heat treatment was found to not alter the nanoporous structure of these carbons, but did significantly decrease their oxygen content. Contact angle kinetics (CAK) and water vapor sorption (WVS) experiments were carried out to determine the wettability of the CICs, before and after heat treatment, showing that the as-synthesized CICs surfaces are much more hydrophilic when compared to commercial carbon black (Vulcan carbon, VC). The high hydrophilicity of the CICs is likely due to their high surface-specific oxygen atomic density ($\sim 10\ \mu mol\ m^{-2}$). Further heat treatment significantly decreases the hydrophilicity of CICs because of the removal of oxygen atoms from their surfaces, as also reflected by their cyclic voltammetric response in acidic solutions.

1. Introduction

Nanoporous carbon materials have attracted extensive interest in recent decades because of their low cost, tunable pore sizes, high specific surface areas, modifiable surface properties, and good electrical conductivity [1–11]. These porous carbon materials are promising candidates as adsorbents, catalyst supports, electrodes in capacitors, etc. As energy sustainability is a critical global objective, the application of nanoporous carbons (with pore sizes between 2 nm and 100 nm) as supports in the catalyst layers of proton exchange membrane fuel cells (PEMFCs) is of great interest [9–16]. Nanoporous carbons have a large surface area to support the catalyst, normally Pt nanoparticles (3–6 nm), and ideally have pores that are large enough to accommodate Nafion ionomeric clusters (to allow for the transfer of protons) and to facilitate the mass transport of H_2, O_2, and water through the catalyst layers [10,11,13].

There are various methods used to fabricate nanoporous carbons [1–3,9], including colloid imprinting [6,11]. In this

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approach, mesophase pitch (MP) is used as the carbon precursor, as it has a high conversion efficiency (up to 85%) to carbon [17], while colloidal silica (CS) is normally used as the templating material. CS suspensions are commercially available and have a narrow particle size distribution. In the synthesis of colloid-imprinted carbon (CIC), MP is imprinted at its softening temperature by dried silica colloids and is then carbonized at high temperatures (e.g., 900 °C). Thus, a reverse porous carbon structure is obtained after the removal of the silica template.

It has been shown that CICs formed in this way have a uniform pore size distribution and dense pore walls, making them promising catalyst supports compared to widely used carbon black and other recently developed ordered mesoporous carbons [10,11]. CICs have also been employed as catalyst supports in fuel cells and as chromatographic supports, giving quite promising results [5,18,19]. CICs can also be applied in lithium batteries, biosensors, capacitors, adsorption systems, etc. [20–24].

Carbon materials can be treated at high temperatures under an inert atmosphere to enhance their degree of graphitization (or crystallinity), in turn increasing their conductivity and stability [25–31]. For example, a high degree of graphitization is believed to elevate the resistance of carbon to the harsh conditions encountered in cathode catalyst layers in PEMFCs [13,32], as shown by Shanahan et al. for heat-treated mesoporous carbons [32].

In most applications, the surface properties of carbon materials, especially their surface polarity (or wettability), significantly impact their performance. For example, surface polarity influences selectivity if carbon is used as an adsorbent [33]. The surface wettability of the carbon materials used in PEMFCs can affect the size distribution and stability of the Pt nanoparticles loaded on them, influence the distribution of Nafion clusters in the catalyst layers [10,15,16,34,35], and can also play a significant role in the overall performance of PEMFCs because of the critical issue of water balance [36–38].

Contact angle measurements are one of the methods widely used to evaluate the surface wettability of materials [39–42]. Generally, a water droplet is deposited on the surface of a material and the profile of the drop is then captured, from which the water contact angle on the surface can be obtained. However, in order to obtain consistent contact angles, these methods require the surface to be as smooth, nonreactive, and homogeneous as possible. These requirements cannot be fulfilled by carbon powders, such as CICs. This is because the interaction between the carbon particles is relatively weak and hence the particles can move under an external force. Thus, it is not possible to employ common contact angle measurements to determine the wettability of carbon powders.

Even so, contact angle kinetics (CAK) have been used recently to examine the wettability of powder samples [43,44]. In this method, the contact of water droplets on the powder is recorded with a camera. The sequential contact angles of a water droplet on the sample surface are then compared with those on another sample at a range of times [43–45], instead of at an arbitrary time, as is the case in normal contact angle measurements [39–42]. The relative wettability of the powder samples can then be determined by comparing the contact angles at each instant time after the water droplet contacts and by considering the contribution of the interactions between the sample particles [42–44]. Additionally, CAK studies of carbon powders using water droplets is expected to give more information than a single contact angle measurement, since the contact process is examined dynamically and in more detail.

Water vapor sorption (WVS) is also widely used to determine the hydrophilic/hydrophobic properties of powder/porous samples [42,46,47], with WVS of carbon samples having been studied in depth by many researchers [48–53]. WVS isotherms can provide important information regarding the suitable relative humidity for the storage of powders and also help to understand the intrinsic surface/interfacial properties of materials [53,54]. A dedicated and well-designed WVS testing system can even reveal the polarity of heterogeneous surfaces [46,53].

In this work, CICs, having a range of pore sizes, were prepared and then heat treated at 1500 °C in a N_2 atmosphere. The relative wettability of the CICs, before and after heat treatment, was then determined by the CAK method, using a high-speed camera to record the initial contacting process of water droplets on pressed CIC powder pellets. A simple method was also used to evaluate the WVS properties of the CIC powders to verify the wettability results obtained from the CAK studies. Along with the CICs, a commercial carbon black (Vulcan carbon) was also treated and examined as a reference using the same methods. The results of this work show that the nanoporous CICs have very durable nanostructures and are relatively hydrophilic, compared to carbon black. Heat-treatment decreases the hydrophilicity of the CICs due to a decline in their surface oxygen content, as confirmed by cyclic voltammetry analysis. It is also shown that CICs with smaller pore diameters are more wettable, following common capillary theory. This work helps to understand the surface chemistry of these template-derived carbons and to assess their potential for use in various applications.

2. Materials and methods

2.1. Preparation of carbons

The synthesis of the colloid-imprinted carbons (CICs) followed procedures published previously [4,6,10,11,31]. Briefly, 1 g of mesophase pitch (MP, Mitsubishi Gas Chemical Company, Inc.) was dispersed in 20 mL of ethanol/H_2O (60:40 v/v), and then a colloidal silica suspension (Ludox-HS-40, Ludox-AS-40, or NanoSol-5050S with an estimated average colloid size of 12 nm, 22 nm, and 50 nm, respectively), containing 10 g of silica, was added drop-wise with vigorous stirring under room conditions. After removing the solvent at elevated temperatures (50–100 °C), the dried SiO_2/MP composite was heated at 400 °C for 2 h and then cooled down to room temperature, followed by carbonization at 900 °C for 2 h, all under N_2 and using a heating rate of 5 °C min^{-1}. The solid product was refluxed in 3 M NaOH solution for at least 24 h to remove the SiO_2 template and to form nanopores, and was then washed with water until it remained neutral. The obtained carbons were named CIC-12, CIC-22, and CIC-50, corresponding to the colloid sizes (in nanometers) used to form their pores.