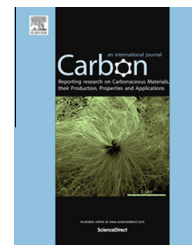


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Comparison of melamine resin and melamine network as precursors for carbon electrodes

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ABSTRACT

Nitrogen-rich carbons synthesized from two melamine-based precursors – a melamine resin (MR) and a melamine network (MN) – were compared based on their pore structure, surface chemistry and electrochemical performance. The effect of carbonization temperatures on carbon pore structure and surface chemistry was investigated by N₂ and CO₂ sorption analyses, potentiometric titration, elemental analysis (CHN) and X-ray photoelectron spectroscopy (XPS). The carbons prepared from melamine resin had higher surface areas and pore volumes than the carbons produced from the melamine network, with carbonization of the MN at temperatures of 700 °C and higher leading to collapse of the MN pore structure. The electrochemical performances of the carbons were evaluated in 1 M H₂SO₄. The changes in carbon surface chemistry after charge–discharge cycles were studied for the two melamine-based carbons carbonized at 800 °C using Synchrotron XPS. This test demonstrated that in two-electrode 1 M H₂SO₄ the redox reactions involving surface nitrogen groups are reversible and redox reactions involving COOH take place. The results revealed the impact of the initial structure of the melamine precursors on the porosity along with the surface chemistry of the carbon matrix on the capacitive performance.

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1. Introduction

Activated carbons from various precursors and activation processes are widely used as electrode materials for supercapacitors due to their large surface area, chemical stability, good electrical conductivity and ability to charge accumulation at the electrode/electrolyte interface [1–3]. They combine a large surface area accessible to electrolyte ions with surface functional groups that influence the formation of the electric

double-layer and promote pseudo-capacitive reactions enhancing electrochemical capacitance [4–6]. Numerous studies have confirmed that the specific capacitance of carbon electrodes is related not only to the carbon's total specific surface area but also to the size and shape of the pores. For example, narrow micropores have been demonstrated to provide optimum electrosorption sites for the formation of electrochemical double-layers with the optimum pore size dependent on the diameter of the solvated electrolyte ions

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[7–9]. However, several studies have also confirmed that mesopores play an important role as ion transport channels in supercapacitor electrodes at high current loads and for fast charge–discharge conditions [10,11].

The capacitive performance of carbon electrodes can be improved by the presence of functional groups, for example nitrogen and oxygen containing groups attached to a carbon matrix [5,12–22]. Functional groups change the electron/donor characteristics of the carbon by a so-called pseudocapacitance energy storage mechanism which is related to reversible Faradaic reactions at the electrode interface [23,24]. For example, positively charged quaternary and pyridine-N-oxide nitrogen groups at the carbon surface are reported to improve electron transfer at high current load and thus to contribute to high capacitance retention [14,25]. The oxidation/reduction reactions contributing to the pseudocapacitance have been found to be from the negatively charged pyrrolic/pyridinic nitrogen atoms in the presence of protons [26] and from a reversible quinone-hydroquinone reaction [4,6,14,27,28]. It is often accepted that oxygen surface groups have an acidic character and exhibit electron acceptor properties, while nitrogen-containing functional groups exhibit basic characteristics with electron donor properties on the carbon surface [29]. However, the origin of the pseudocapacitance effect of nitrogen and oxygen groups is still not fully understood. Furthermore the influence of functional groups on the capacitance of carbon materials depends not only on their distribution and concentration on the surface, but also on the combination of groups present and their location in the carbon pore system [5,30].

In this paper we compare the effects of porosity and surface chemistry on the capacitance of nitrogen-containing carbons obtained from two melamine precursors: a non-porous melamine resin and a porous melamine network [31,32], which contain 45 wt.% and 41 wt.% nitrogen, respectively. Carbons derived from melamine precursors have been applied as electrodes for supercapacitors due to their high content of surface nitrogen with porous structure [30,33–35]. The results are discussed in terms of how the structure of the melamine precursors and the conditions of the thermal treatment affect the porosity and the surface chemistry of the corresponding carbons, and thus cause the differences in their electrochemical performances in an aqueous electrolyte. The surface chemistry of the melamine-based carbon electrodes upon electrochemical tests in a two-electrode supercapacitors setup in acidic electrolyte is investigated. This work brings broader understandings of the combined effects of porosity and surface functionalities of carbon materials on their performance as supercapacitors.

2. Experimental

2.1. Preparation of the melamine-based carbons

Carbons with incorporated nitrogen surface functional groups were prepared in a two-step process involving (1) the synthesis of nitrogen-rich precursors and (2) the carbonization of the precursors at temperatures from 600 to 1000 °C. The melamine resin (MR) was prepared following the procedure

described by Hulicova et al. [33] with the exception that in this study we did not use the expandable fluorine mica as a template. The melamine network (MN) was synthesized from melamine and terephthalaldehyde (99%, Sigma Aldrich) by a modified version of the procedure reported by Schwab et al. [31]; in our experiment the reaction was performed in air instead of in an inert atmosphere. The carbon products are labeled according to the melamine precursor and the carbonization temperature: for example, MR600 is the carbon prepared from the melamine resin at 600 °C. Details of the synthesis methods are provided in the [Supporting Information](#).

2.2. Evaluation of physical and chemical properties

The porous textures of the melamine-based carbons were characterized by N₂ sorption at –196 °C (Quadrasorb SI, Quantachrome) and CO₂ adsorption at 0 °C (TriStar II 3020, Micromeritics). The specific surface area accessible to the N₂ molecule, S_{NLDFT} , and corresponding pore size distributions (PSDs) were calculated from the N₂ isotherms using a non-local density functional theory (NLDFT) algorithm for carbon slit pores included in the Quadrasorb software. Total pore volumes V_t were calculated from N₂ isotherms at relative pressures of $P/P_0 = 0.98$. The micropore surface area S_{mic} and micropore volume V_{mic} for pores less than 1.0 nm were calculated from CO₂ adsorption isotherms using the Dubinin–Radushkevich (DR) equation [36]. Micropore PSDs were also calculated from CO₂ sorption isotherms using a density functional theory (DFT) model for carbon slit pores (TriStarII 3020 V1.03).

The contents of carbon, hydrogen and nitrogen in the melamine-based carbons were measured with a FlashEA1112 Series CHN analyzer equipped with a thermal conductivity detector. The oxygen content was calculated from a material balance with the assumption that the melamine-based carbons were ash free. Surface functional groups on the carbons were characterized using X-ray photoelectron spectroscopy (XPS, ESCALAB220i-XL VGScientific, UK), potentiometric titration and the measurement of the carbon pH. To investigate the changes in surface chemistry of the melamine-based carbon electrodes upon electrochemical measurements a second set of high-resolution XPS measurements, which are referred to in this manuscript as the Synchrotron XPS, were carried out on the Soft X-ray Spectroscopy beamline (14ID) of the Australian Synchrotron in Melbourne, Australia. The [Supporting Information](#) provides details for each of these techniques including the data analysis protocols applied to the XPS data.

2.3. Electrode preparation and electrochemical measurements

Sandwich-type electrochemical cells were constructed with two symmetrical carbon electrodes – prepared from 90 wt.% of active materials, 5 wt.% of carbon black and 5 wt.% of poly(vinylidene fluoride) (PVDF) – separated by glass microfiber paper. The electrodes were immersed in 1 M H₂SO₄ electrolyte under a vacuum. Cyclic voltammetry (CV) and galvanostatic charge–discharge cycles were measured in the voltage range 0–1 V on a Solartron 1480 Multistat. The

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