



New insights into the electrochemical behaviour of porous carbon electrodes for supercapacitors

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ABSTRACT

Activated carbons, with different surface chemistry and porous textures, were used to study the mechanism of electrochemical hydrogen and oxygen evolution in supercapacitor devices. Cellulose precursor materials were activated with different potassium hydroxide (KOH) ratios, and the electrochemical behaviour was studied in 6 M KOH electrolyte. *In situ* Raman spectra were collected to obtain the structural changes of the activated carbons under severe electrochemical oxidation and reduction conditions, and the obtained data were correlated to the cyclic voltammograms obtained at high anodic and cathodic potentials. Carbon-hydrogen bonds were detected for the materials activated at high KOH ratios, which form reversibly under cathodic conditions. The influence of the specific surface area, narrow microporosity and functional groups in the carbon electrodes on their chemical stability and hydrogen capture mechanism in supercapacitor applications has been revealed.

1. Introduction

Porous carbons have been extensively exploited in electrochemical applications including gas storage and separation, catalyst supports and energy conversion and storage electrodes [1,2]. Carbon is the most versatile element on earth with the highest catenation power and when combined with other atoms, leads to materials with unique properties including high specific surface area, tuneable chemical structure/functional groups, electronic and ionic conductivity, lightweight and more. Due to all these unique features, carbon materials are ideal candidates for energy conversion and storage devices [3]. Activated carbons, a special class of amorphous microporous carbons, have been intensively used as supercapacitor electrode materials, as well as to store hydrogen by controlling the resulting microporosity and surface chemistry [4–8]. The role of the factors above and their importance in the electrochemical hydrogen storage mechanism have been previously discussed [9–11]. Nanostructured carbons have gained increasing

interest as a promising alternative for electrochemical energy storage systems in aqueous media; however, the fine-tuning of the pore structure and surface functionality is yet to be fully addressed [10]. It was found that the hydrogen uptake increases with narrow microporosity and an increase in unsaturated carbon atoms, i.e. low content in surface oxygen functionalities, favours electrochemical storage of hydrogen via the electroreduction of water in basic media [12]. Ultra-microporosity also plays an important role in hydrogen uptake and storage, whereby a hierarchical porous structure consisting of meso- and macro-pores can provide the mass transport channels to the smaller pores, which therefore provide excellent capacity retention and promising features for electrochemical hydrogen storage applications [13]. In addition, the presence of functional groups has previously been proven to affect the hydrogen adsorption mechanism negatively, whereby the trapping of the nascent hydrogen atoms decreases upon increasing the amount of surface oxygen groups. It was suggested that active sites that are saturated with oxygen groups cannot contribute to the hydrogen trapping

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mechanism, given that the porosity is kept constant [12].

Levy-Garcia et al. reported that carbon-hydrogen bonds form reversibly when using KOH-activated carbon materials from anthracite and commercial activated carbons in different aqueous media under cathodic conditions [14]. *In situ* Raman spectroscopy and surface chemistry characterization *via* temperature programmed desorption (TPD) technique were employed in this study and it was found that the surface functionality and porous texture play a major role in determining the electrochemical hydrogen storage process [12]. The efficient process of hydrogen storage in activated carbons has proven to be more efficient than in carbon nanotubes or other methods, including pressure and cryogenic conditions, due to the easy penetration of nascent hydrogen produced in the electrolyte into the porous carbon network [15,16]. However, a direct correlation between the structural properties, presence of functional groups, pore size distribution and wettability of nanocarbons and reversible hydrogen chemisorption and storage has not yet been identified [1]. Hence, there is a vital need to better understand the hydrogen/energy storage in supercapacitor devices in order to improve their performance in terms of reversibility of the porous electrode material.

Carbon/carbon supercapacitors belong to the class of electrical double-layer capacitors (EDLCs), where energy is stored *via* charge separation at the electrode/electrolyte interface [17]. The charge storage mechanism excludes any pseudocapacitive behaviour, and the electrolyte ions are electrostatically and reversibly adsorbed in the double-layer of the porous networks of the carbon electrodes. However, in the case of surface functionalities, Faradaic processes may arise that comprise of reversible reactions between the functional groups at the accessible electrode surface and electrolyte ions. Hence, the pore size distribution, porosity and functional groups content can be tuned to optimize the electrochemical performance of supercapacitors. Nanostructured electrodes have gained increasing popularity as the manipulation of narrow microporosity and surface functional groups leads to an enhancement in the gravimetric capacitance, as well as self-discharge mechanism (the relaxation of potentials across the elements of the porous electrodes) in supercapacitors, hence increasing the energy and power densities of carbon materials [18,19]. The non-ideal polarization of carbon surfaces, due to surface oxidation reactions and possible intercalation processes, specifically upon cathodic polarization, makes fundamental understanding of the electrochemical processes occurring very challenging [18]. The behaviour of EDLCs is surface specific, whereby adsorption interactions between oxygen species on the carbon surface and electrolyte ions occur. The identification of surface functionalities on carbon surfaces and their effect on potential-of-zero-charge, the contact angle between electrode/electrolyte interface and wettability of electrode materials, have been studied previously *via in situ* X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and Fourier transform infrared (FTIR) techniques [20–23]. However, and to the authors' best knowledge, this is the first time that *in situ* Raman spectroscopy has been employed to study the extreme anodic and cathodic conditions that activated porous carbon electrodes can endure for supercapacitor applications, which is correlated to the porous structure and oxygen content.

This work allows the investigation of the effect of different pore sizes and surface functional groups at the highest possible potentials applied prior to undesirable gas evolution at anodic and cathodic conditions. The crucial relationship between the electrode structure and the applied potentials would grant the application of wider potential limits in aqueous systems and therefore achieving better supercapacitor electrochemical performance in terms of energy and power delivery. This study opens a platform to i) understand the behaviour of different carbon electrodes at extreme conditions and ii) correlate the surface and morphological effects of different porous structures to the electrochemistry in order to avoid the electro-reduction and/or electro-oxidation processes.

2. Experimental

2.1. Carbon activation

Chemical activation of softwood Kraft cellulosic pulp (UPM-Kymmene Corporation, Finland) with different KOH loadings was conducted under a nitrogen atmosphere at a flow rate of 1 L min⁻¹ heating ramp of 20 °C min⁻¹ up to 850 °C with a dwell time of 1 h, as reported elsewhere [24]. Briefly, the cellulose of 500 g m⁻² areal density was soaked in different concentrations of KOH solutions and dried in a vacuum oven overnight prior to the carbonization process. The KOH / cellulose weight ratios used were: 0.005:1, 0.01:1, 0.1:1, 0.5:1, 1:1, 2:1 and 3:1. All samples are denoted as KOH -*n*, with *n* representing the weight ratio of KOH/cellulose.

2.2. Characterization of porous texture and surface chemistry

The surface structure of the carbonized samples was characterized with scanning electron microscopy (SEM) at 10 kV in the secondary electron imaging mode (EVO MA10, ZEISS, Germany) and transmission electron microscopy (TEM) with 200 kV accelerating voltage (JEOL, JEM-2100, UK). The porous texture of the eight samples was characterized with nitrogen adsorption-desorption isotherms at 77 K (3Flex Surface and Catalyst Characterization System, Micromeritics, USA) and carbon dioxide adsorption isotherms at 273 K (Autosorb-6, Quantachrome) that followed sample degassing at 200 °C overnight (VacPrep 061 Sample Degas System, Micromeritics, USA). The total pore volume was determined at a relative pressure (P/P_o) of 0.99, and the microporous contribution was evaluated using the non-local density functional theory (NLDFT) method to the N₂ adsorption on carbon slit pores [25,26]. Micromeritics ASAP 2010 software was used to interpret the data acquired for each sample. The ultra-micropore volume (with pore sizes < 0.7 nm) were calculated using the Dubinin-Radushkevich (DR) method at relative pressures below 0.025 from the CO₂ adsorption isotherms. The densities of the adsorbed phases, N₂ and CO₂, used were 0.808 g cm⁻³ and 1.023 g cm⁻³. Specific surface areas (SSA) were obtained by applying the Brunauer-Emmet-Teller (BET) method, calculated at relative pressure range between 0.001 and 0.2. The macropore size distribution and total macropore volume of the carbonized samples were determined using mercury intrusion porosimetry (MIP) (Poremaster, Quantachrome Instruments, USA).

The surface chemistry of the carbon materials was assessed using temperature programmed desorption (TPD) conducted in a DSC (differential scanning calorimetry)-TGA (thermogravimetric analysis) instrument (TA Instruments, SDT Q600 Simultaneous) coupled with a mass spectrometer (Thermostar, Balzers, GSD 300 T3). 5 mg of each sample were heated up to 950 °C at a heating ramp of 20 °C min⁻¹ under a helium flow rate of 100 ml min⁻¹. To further analyse the surface chemistry in the different carbon materials, X-ray photoelectron spectroscopy (XPS) measurements were obtained on a K-ALPHA Surface Analysis spectrometer (Thermo Scientific) with monochromatic aluminium K α as the excitation source. CasaXPS software was used to analyse the changes in binding energy of C_{1s} peaks corresponding to different activated carbons and provide detailed information on the surface functionalities and individual carbon peaks. The oxygen/carbon ratios were determined from the C_{1s} and O_{1s} peaks and using Shirley background subtraction.

The wettability behaviour of the various activated carbons has been determined by measuring the contact angle between water and the surface of the prepared carbon electrodes (95:5 wt.% carbon: polytetrafluoroethylene) using First Ten Angstroms (FTA) 1000 B Drop Shape Analyzer (First Ten Angstroms Inc., USA). The contact angle was measured using the software FTA32 Video 2.1.

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