

INFLUENCE OF PORE TEXTURE OF CARBON XEROGELS ON THEIR BEHAVIOR AS ANODES FOR LI-ION BATTERIES

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Introduction

Carbon materials are widely used as anodes for Li-ion batteries due to their low cost and availability. Among these, graphite is the most widespread, but increased energy density and lifetime are expected from hard carbons due to their 3D porous architecture. Such materials however generally suffer from high irreversible losses during the first charge-discharge cycle and the influence of porosity on the electrochemical behavior still remains an open debate. This study aims at determining which textural parameters of porous carbons can explain some observed electrochemical features. For that purpose, carbon xerogels are extremely interesting since their textural parameters can be independently controlled and tailored through the synthesis conditions. Carbon xerogels (CX), prepared from resorcinol-formaldehyde mixtures, can be described as microporous nodules linked together to form meso- or macroporous voids inside a 3D gel structure; the size of these voids can be tuned by changing the synthesis conditions without affecting other parameters such as the micropore volume. On the opposite, the microporous fraction of a given macroporous carbon xerogel can be independently increased upon activation (*e.g.* by physical CO₂ treatment), or reduced upon coating the nodules with an additional carbon layer, by CVD for instance.

Materials and Methods

Carbon xerogels displaying various meso-or macropore sizes were prepared from aqueous resorcinol-formaldehyde mixtures in presence of Na-carbonate for the adjustment of the pH. After ageing and drying under vacuum, the dry organic gels were ball-milled in order to produce a powder with particle sizes centred on 10 µm. The powders were then pyrolyzed under N₂ atmosphere at 900°C to produce the carbon xerogels. Physical activation was carried out subsequently to the pyrolysis step upon switching the atmosphere to CO₂, still at 900°C, for different durations in order to increase the micropore volume of the materials. Chemical vapor deposition of ethylene on a pyrolyzed CX was performed in a stainless steel tubular oven at 685 °C, followed by a heat treatment at 900°C under inert atmosphere.

After grinding and pyrolysis, the materials were processed into electrodes, either by bar-coating of an organic ink with PVDF as a binder and NMP as a solvent, or by spraying an aqueous slurry containing of a water-soluble binder. This latter technique was necessary to keep the micropores accessible. After drying under vacuum at 120°C, the formed electrodes were directly introduced into a glovebox.

Textural parameters of the CX (and the composites formed between the CX and the binder) were characterized by N₂ adsorption and Hg porosimetry. The electrochemical measurements were carried out in CR2032 coin cells, where the tested material acted as positive electrode and a Li-metal disk as the negative, reference and counter electrode. A Celgard[®] separator soaked with electrolyte (LP71) was placed in-between. The cell assembly was performed in an Ar-filled glove-box. Charge-discharge cycles were recorded at C/10 (*i.e.* using the necessary current to charge completely the battery in 10 h, based on the theoretical value for graphite – 372 mAh.g⁻¹) between 0.005 and 1.5 V or 3.0 V *vs.* Li⁺/Li with a potentiostat or a battery tester (at a controlled temperature of 25°C).

Results and Discussion

In a first instance, all parameters such as micropore volume, particle sizes and E-C testing conditions were kept constant, in order to isolate the sole influence of the meso- or macropore texture on the electrochemical behavior¹. Five carbon xerogels displaying various pore sizes, pore volumes and meso/macropore surface areas, were evaluated as anodes for Li-ion batteries in half-cell configuration. Capacitance measurements have brought to light the very limited wettability of micropores by the electrolyte that remains at the external surface of CX nodules. In that respect, a clear relationship could be established between the external surface area of the nodules, *i.e.* which is accessible to the electrolyte, and the charge/discharge capacities (**Figure 1a**). The importance of an in-depth textural characterization of the active material-binder composite has also been pointed out, since the presence of the binder in the electrode strongly affects the micropore volume of the porous carbon.

In a second step, the influence of microporosity has been evaluated². Post-synthesis treatments aiming at modulating the microporosity *only* have led to a series of materials with total surface areas comprised between 200 and 2300 m².g⁻¹, with nearly constant macropore size and volume. Considering the Li⁺ insertion during the first cycle, a clear linear relationship with the increase of the volume of supermicropores (0.7 – 2 nm) is observed (**Figure 1b**), indicating an increased storage capacity with micropore enlargement by activation. The reversible de-insertion capacity nevertheless remains constant when the maximum potential value is set at 1.5 V *vs.* Li⁺/Li. If however the de-insertion is carried out up to a maximum potential value of 3.0 V *vs.* Li⁺/Li, a clear linear relationship can be evidenced between the supermicropore volume and the reversible capacity. These results suggest that the contribution of the larger micropores of CX materials to the observed Li⁺ storage capacity is significant when cycling is performed in a wider potential window *and* when a water-compatible binder is used for the electrode preparation, in order to preserve the access to this fraction of the material's porosity³. It can be proposed that, during the first discharge, the Li⁺ ions are massively inserted within the CX micropore structure, but can only be partially extracted when charging up to 1.5 V *vs.* Li⁺/Li. Much more significant deinsertion from the internal part of the activated CX can only be achieved upon increasing the potential up to 3.0 V *vs.* Li⁺/Li. This also demonstrates that the electrochemical testing conditions could strongly affect the conclusions regarding the performance of porous hard carbons, especially when comparisons are mainly based on the capacity values.

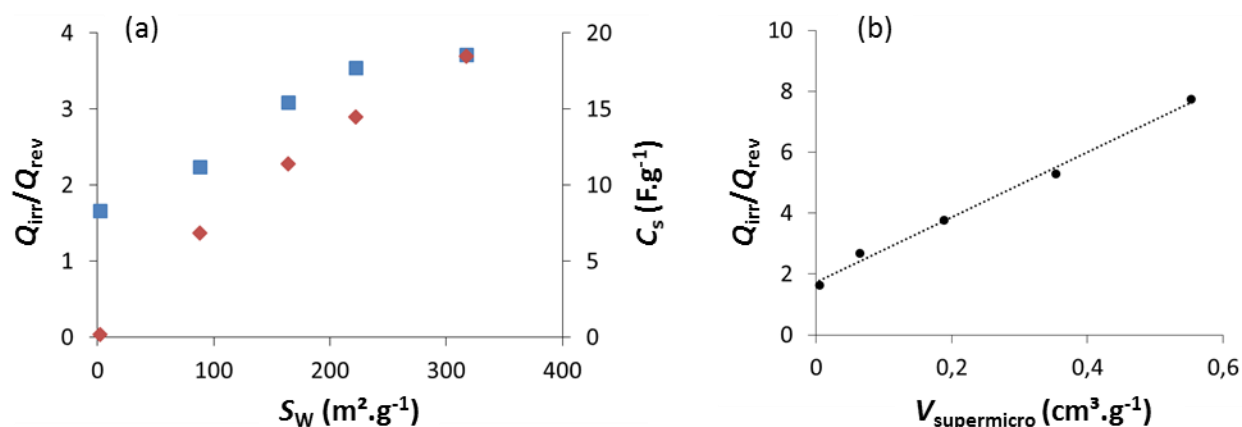


Figure 1. Electrochemical behavior of composite electrodes made of carbon gels; the electrolyte is identical in all cases (LP71, *i.e.* 1 M LiPF_6 in a mix of carbonates). (a) Relationship between the external surface area of the carbon nodules, S_w , and (■) the $Q_{\text{irr}}/Q_{\text{rev}}$ ratio (half-cell Li-ion battery configuration, maximum voltage of 1.5 V vs. Li^+/Li , cycles recorded at C/10) and (◆) the specific capacitance, C_s (measured by cycling at 20 mV s^{-1} from -0.3 to 0.3 V); PVDF was used as a binder¹. (b) $Q_{\text{irr}}/Q_{\text{rev}}$ at the first cycle as a function of the calculated cumulative volume of supermicropores, *i.e.* 0.7–2.0 nm (half-cell Li-ion battery configuration, maximum voltage of 1.5 V vs. Li^+/Li , cycles recorded at C/10); xanthan gum was used as a binder².

Conclusions

Carbon xerogels are interesting materials to help understanding the individual contribution of different pore textures on the electrochemical behaviour when applied as anodes for Li-ion batteries. This study in particular also demonstrates the importance of the electrode preparation pathway in order to preserve the pore texture of the starting material. Finally, the conditions of EC measurements need also to be taken into account when comparing results from different studies.

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