

Carbon Xerogels as Model Materials to Study the Behavior of Hard Carbons as Anodes for Lithium-ion Batteries

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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 architectures. 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, 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.

In that respect, a first study has been realized by controlling and keeping constant all parameters such as micropore volume, particle sizes and E-C testing conditions, in order to isolate the sole influence of the meso- or macropore texture on the electrochemical behavior [1]. For that purpose, a series of five carbon xerogels displaying various pore sizes, pore volumes and meso/macropore surface areas, were synthesized and 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 carbon xerogels 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. Moreover, the importance of an in-depth textural characterization of the active material-binder composite has also been pointed out. Indeed, the presence of the binder in the electrode strongly affects the textural parameters of the porous carbon, mainly the micropore volume.

In a second step, the influence of microporosity has been evaluated [2]. To achieve this purpose, two conditions were required: (i) the use of a method to prepare electrodes that allows to preserve the micropore texture of the pristine materials and (ii) techniques to modulate the micropore fraction of the materials. The first condition was met upon coating the active material *via* an original aqueous process that indeed allows to maintain the textural characteristics of the CX powders in the final active material-binder composite, which is not the case when PVDF in NMP is used [3]. The modulation of microporosity was realized upon applying post-synthesis treatments such as CO₂ physical activation and CVD by ethylene cracking. Following these procedures, a series of materials with surface areas, S_{BET} , comprised between 112 and 2234 m².g⁻¹ and nearly constant macropore size and volume were produced. In this case, capacitance measurements performed on activated CX show a significant improvement of the wettability of the materials by the electrolyte used for E-C characterization, whereas the opposite was observed on the CVD-treated sample. A clear relationship was observed between the specific surface area of the samples, S_{BET} , and the reversible and irreversible capacity at a maximum potential value of 3 V *vs.* Li⁺/Li. These results indicate that the contribution of the microporosity of CX materials to the observed Li⁺ storage capacity is significant when cycling is performed in a wider potential window and when an aqueous compatible binder is used for the electrode preparation. Whereas Li⁺ ions are only partially extracted when the charge of the half-cell is performed up to 1.5 V *vs.* Li⁺/Li, the increase of this potential value up to 3 V *vs.* Li⁺/Li allows for a more significant de-insertion of the Li⁺ ions from the internal part of the activated CX. This demonstrates that the electrochemical tests conditions could strongly affect the conclusions regarding the performances of porous hard carbons.

[1] M.-L. C. Piedboeuf, A.F. Léonard, F.L. Deschamps and N. Job, 2016, *J. Mater. Sci.*, **51**, 4358-4370.

[2] M.-L. C. Piedboeuf, A.F. Léonard, C. Balzers, G. Reichenauer and N. Job, 2017, *to be published*.

[3] N. Rey-Raap, M.-L. C. Piedboeuf, A. Arenillas, J. A. Menéndez, A.F. Léonard and N. Job, 2016, *Mater. Des.*, **109**, 282-288.