

RESORCINOL-FORMALDEHYDE CARBON XEROGELS AS LITHIUM-ION BATTERY ANODE MATERIALS: INFLUENCE OF POROSITY ON CAPACITY AND CYCLING BEHAVIOUR

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Introduction

Carbon xerogels are promising candidates in the development of new high performance C-based anode materials for Li-ion batteries. Indeed, their specific capacities widely exceed that of conventional graphitic structures, and they can be intercalated/deintercalated in a low-cost electrolyte based on propylene carbonate (PC), which has an excellent conductivity at low temperatures. In addition, such carbonaceous materials show very small changes of volume during the charge/discharge, providing a long cycle life of such an anode. Nevertheless, hard carbons also exhibit quite high irreversible capacity losses due to their intrinsic high microporosity and, compared to graphite, a poor rate performance related to slow diffusion of Li in the internal structure [1]. To reduce these disadvantages, the structural and textural characteristics need to be carefully controlled.

Porous carbon xerogels can easily be prepared from resorcinol-formaldehyde mixtures, which are polymerized, dried and pyrolysed. Following this route, very pure carbon materials can be obtained, on contrary of materials derived from natural precursors, such as active charcoals. The inherent porosity of C-xerogels can be described as microporous nodules between which meso- or macroporous voids exist, the size of the latter being mainly controlled by the pH of the precursor solution as well as by the drying procedure [2-4]. The presence of this considerable meso- or macropore volume makes these materials superior in terms of reduced diffusion limitations. Nevertheless, too a high microporosity often leads to considerable irreversible capacity losses due to entrapment of Li⁺ ions during the first charge/discharge cycle. Also, the size of the mesopores is important since too small openings between the microporous nodules hinder the diffusion of lithium ions within a bulk electrode material. For these reasons, all of the porosity levels of porous carbon xerogels have to be carefully controlled if they are to be used as components of anodes for Li-based batteries.[5-6]

The goal of this work is to shed some light on the effect of the different pore size levels of carbon xerogels on the electrochemical characteristics and behavior when applied as anode materials. To reach this target, xerogels presenting various pore sizes were prepared. Their textural features were investigated in detail, followed by the in-depth determination

of performance as anode in CR2016 ($\varnothing = 20$ mm, h = 1.6 mm) Li-ion coin cells.

Experimental

The aqueous organic gels were synthesized by polycondensation of resorcinol (R) with formaldehyde (F) in water. In a typical synthesis, 9.91g of resorcinol is dissolved in 18g of deionized water, the pH of which is adjusted either by addition of H₂SO₄ or Na-carbonate. 13.5 ml of a 37% solution of formaldehyde was then added and the mixture magnetically stirred for 1 h. In each case, the R/F molar ratio was fixed to the stoichiometric value (0.5). The obtained homogeneous gel precursor solutions were then sealed in autoclavable flasks and aged for 3 days at 85°C, followed by vacuum drying at 60 and 150°C over a period of 30 h. The dry monolithic organic polymers were then pyrolysed under inert atmosphere at 800°C.

The textural characterization of the samples was performed by nitrogen adsorption-desorption isotherms at -196°C on a Carlo Erba Sorptomatic 1900 from Fisons Instruments after outgassing the samples at room temperature at 10⁻⁴ Pa. The Dubinin-Radushkevich (DR) method was applied to obtain the narrow micropore volume, the specific surface area was calculated by the BET equation and the total micro- and mesopore volume was assessed by N₂ adsorption at saturation. For samples containing large mesopores and macropores, the mercury porosimetry was used to determine average pore size as well as the total pore volume. The measurements were performed with a Carlo Erba Pascal 140 and 240 after outgassing under primary vacuum.

For electrochemical characterization, the samples of carbon xerogels were crushed and sieved through a 45µm sieve for making electrodes. The active materials were mixed with the amount of 8% polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP) solution. The resulting slurry was cast onto the copper foil, and a doctor blade with a gap opening of 200µm was used to define the maximum thickness of the freshly coated layer. The resulting film was dried at 120°C in order to evaporate the NMP. The disc electrodes of 16 mm diameter were obtained from a coated copper foil current collector using a punch. Before assembling the cell, the electrodes were dried under primary vacuum at 120°C during 12h. The coin cells (CR2016 standard size) were assembled in an argon filled glove box. The TEKLON™ EDEX separator and the electrolyte Selectipur LP71 (EC:DEC:DMC 1:1:1, 1M LiPF₆, Merck) were used for assembling the coin cells. The coin cells were investigated by galvanostatic charge-discharge in the potential range 1.5V to 0.005V vs. Li at C/20 rate (theoretical capacity of 372 mAh/g).

Results and Discussion

The textural features of the different samples are listed in Table 1. As can be seen, the materials exhibit different features with respect to the starting synthesis pH. Samples ML-1 and ML-2 are prepared in slightly acidic media and show very close specific surface area and micropore volume. The sole difference relies in their pore sizes which increase

from 15 to 85 nm upon decrease of pH. Sample ML-3, prepared in strong acidic medium (H₂SO₄ pH 0.5) is very different with very low specific surface area and micropore volume but very large macropore size.

Table 1 Textural features of the different carbon xerogels

| Sample | pH | S _{BET} (m ² /g) | V _{micro} (cm ³ /g) | Ø (nm) |
|--------|-----|--------------------------------------|---|--------|
| ML-1 | 6.5 | 682 | 0.27 | 15 |
| ML-2 | 5.8 | 643 | 0.26 | 85 |
| ML-3 | 0.5 | 48 | 0.02 | 5000 |

Table 2 shows the information about the density of the tested samples. All of them exhibit quite a low tap density, which could lead to a bad adhesion of active materials on the copper current collector. In order to improve the quality of the anodes, the electrodes were compacted to the desired density first by impressing, then by calendaring. The average density of the carbon layer after calendaring ranges between 0.3 and 0.6 g/cm³. Even after this step however, the sample ML-2 shows a density that remains too low for being appropriate as anode material. The quantity of active material on the anode was estimated to be in the range of 4-5 mg/cm² and the thicknesses before and after calendaring were in the range of 0.120-0.150 mm and 0.06-0.08 mm respectively.

Table 2 Density of electrode materials

| Sample | Tap density (powder) (g/cm ³) | Impressed electrode density (g/cm ³) | Electrode density after calendaring, (g/cm ³) |
|--------|---|--|---|
| ML-1 | 0.45 | 0.38 | 0.56 |
| ML-2 | 0.18 | 0.21 | 0.32 |
| ML-3 | 0.48 | 0.30 | 0.64 |

The galvanostatic charge/discharge curves for these materials were analyzed at C/20 current rate within the range of cut off potentials from 0.005V to 1.5V. These conditions are typically used for testing graphite material, usually employed as anode material in Li-ion secondary batteries. The reversible and irreversible mass capacities for the two first lithium insertion/deinsertion cycles are shown in table 3.

Table 3 Electrochemical performance of carbonaceous materials at current density C/20

| Sample | First cycle | | Second cycle | |
|--------|------------------------|--------------------------|------------------------|--------------------------|
| | Rev. capacity (mA·h/g) | Irrev. capacity (mA·h/g) | Rev. capacity (mA·h/g) | Irrev. capacity (mA·h/g) |
| ML-1 | 270 | 923 | 222 | 49 |
| ML-2 | 341 | 1074 | 292 | 89 |
| ML-3 | 332 | 238 | 323 | 16 |

The corresponding first and second charge/discharge profiles of the tested samples are shown in figures 1-3.

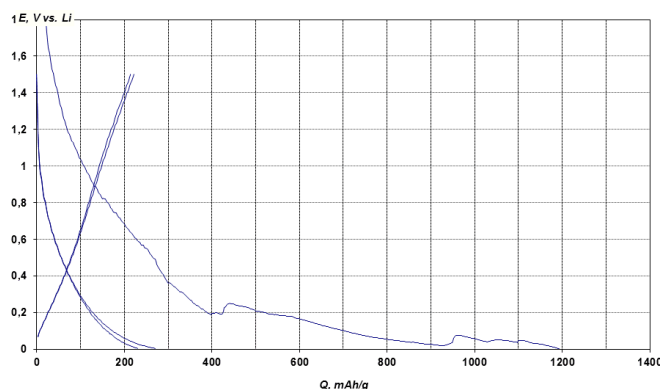


Fig. 1 Typical plots of voltage vs. capacity of ML-1 as negative electrode in a Li/ML-1 cell during the first and second charge (Li-extraction) / discharge (Li-insertion) cycles at C/20.

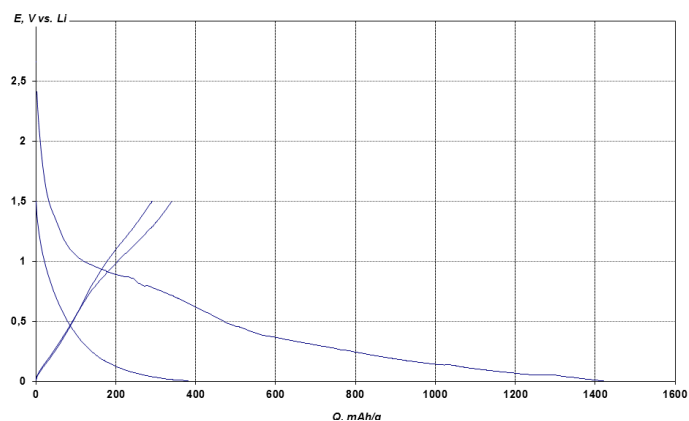


Fig. 2 Typical plots of voltage vs. capacity of ML-2 as negative electrode in a Li/ML-2 cell during the first and second charge (Li-extraction) / discharge (Li-insertion) cycles at C/20.

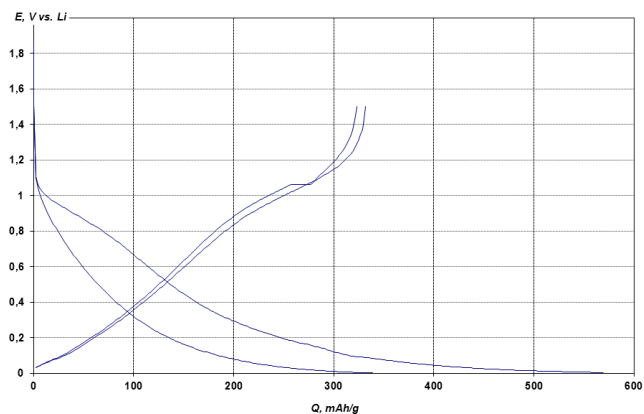


Fig. 3 Typical plots of voltage vs. capacity of ML-3 as negative electrode in a Li/ML-3 cell during the first and second charge (Li-extraction) / discharge (Li-insertion) cycles at C/20.

All the samples show a large value of irreversible capacity during the first cycle. This phenomenon can be related to two contributions: (i) the entrapment of lithium within the micropores and (ii) the formation of the solid electrolyte interface (SEI). Nevertheless, the sample ML-3 has an irreversible capacity of 238 mAh/g which is much lower than the two other samples. This very big difference could be explained by the fact that this sample presents a much lower micropore volume and specific surface area leading to less irreversible entrapment of lithium during the first loading. As far as reversible capacity is concerned, sample ML-1 shows the smallest capacity for both the first and the second cycle. This could be attributed to the fact that this material possesses the smallest pore size, demonstrating the importance of providing a good access within the framework. Nevertheless, this statement would have to be confirmed by testing materials with intermediate mesopore sizes. For the second cycle, the irreversible capacity is considerably reduced except for sample ML-1 that shows the smallest density whereas the reversible capacity stays at values higher than 220 mAh/g. On contrary, the low surface area macroporous sample ML-3 shows the best reversible capacity after the second cycle, with values approaching that of commonly used graphite. For example, when cycled at a rate of C/20 for 10 cycles, this sample shows a capacity of 320 mAh/g; the value is kept at 200 mAh/g when increasing the rate up to C/5.

Figure 4 shows the cycling performance of ML-3 between 0.005 and 1.5V at current rate C/5.

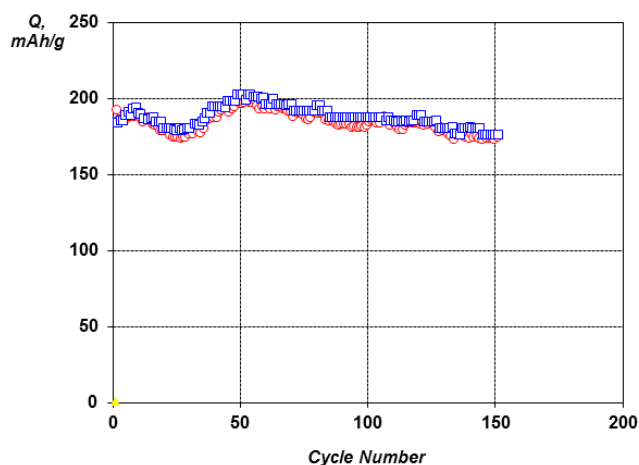


Fig. 4 Cycling performance of ML-3 at C/5

The long-term cycling performance was investigated by cycling the anodes at C/20 and C/5. The capacities observed for ML-1 and ML-2 fall rapidly, but again, the macroporous sample ML-3 exhibits best capacity retention upon cycling and invariable discharge capacity of ~175 mAh/g after more than 100 cycles.

Conclusions

These first results show that carbon xerogels are very promising candidates as anode materials for Li-based batteries, provided the textural characteristics are carefully controlled. In this contribution, we tried to establish a relationship between the micropore volume, specific surface area and meso- or macropore sizes and the electrochemical performances of carbon xerogels when applied as anode. As expected, materials with high amount of micropores lead to very high losses of lithium during the first insertion/deinsertion cycle, revealing that such materials are not appropriate at all for being used in secondary battery assemblies. On the opposite, the material with very low micropore volume and specific surface area shows interesting performances that approach those of conventionally used graphite. This study has also shown the beneficial effect on increasing the mesopore sizes towards larger values with better reversible capacities.

From all these results, it appears that porous carbon xerogels could very well become an interesting alternative to conventionally used graphite in lithium based batteries, mainly because of their easy synthesis, tunable textural characteristics and chemical purity, provided the irreversible capacity can be further reduced, i.e. the micropores widely suppressed.

The next steps will be to detail this study by performing the electrochemical testing of materials presenting intermediary textural characteristics between those presented in this work. In that way, establishing a complete relationship between the porosity and the electrochemical performance should be possible.

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References

- [1] S. Flandrois, B. Simon, *Carbon* 1999; 37; 165.
- [2] N. Job, A. Théry, R. Pirard, J. Marien, L. Kocon, J.-N. Rouzaud, F. Béguin, J.-P. Pirard, *Carbon* 2005; 43; 2481.
- [3] C. Lin, J.A. Ritter, *Carbon* 1997; 35; 1271.
- [4] N. Job, R. Pirard, J. Marien, J.P. Pirard, *Carbon* 2004; 42, 619.
- [5] F. Cheng, Z. Tao, J. Liang, J. Cheng, *Chem. Mater.* 2008; 20; 667.
- [6] K.T. Lee, J.C. Lytle, N.S. Ergang, S.M. Oh, A. Stein, *Adv. Funct. Mater.* 2005; 15; 547