

TURNING LOW-VALUE COAL TAR DERIVED LIQUIDS INTO CARBONACEOUS MATERIALS AS ANODES FOR LI-ION BATTERIES

Alberto Castro-Muñiz^{1*}, Alexandre F. Léonard², Sara Lorenzo-Fierro, Amelia Martínez-Alonso, Juan M.D. Tascón, Fabián Suárez-García, Nathalie Job², Juan I. Paredes

¹ Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain.

² University of Liège, Department of Chemical Engineering – Nanomaterials, Catalysis, Electrochemistry – Institute of Chemistry (B6a), 4000 Liège, Belgium.

*Presenting author's e-mail: alberto@incarcsic.es

Introduction

In current Li-ion batteries, graphite remains the most common anode material. However, its theoretical capacity is limited to 372 mA h/g, *i.e.* 1 Li ion per 6 C atoms.¹ Much higher capacity values can be potentially attained with the so-called hard carbons. Among these, ordered mesoporous carbons (OMCs) represent a particularly attractive class of materials owing to their highly regular mesostructure. It has indeed been reported that such materials could exhibit specific capacities up to 1100 mA h/g with good cycling stability, which has been attributed to their regular mesoporous structure being favorable to impregnation by the electrolyte.^{2, 3} Furthermore, silica (SiO₂) can be used as a high-capacity anode material for Li-ion batteries. Indeed, a large theoretical capacity of 1965 mA h/g can be expected for this compound. However, despite interesting features such as low-cost, environmental friendliness and natural abundance, its poor electronic conductivity and large volume variation upon cycling has hampered its use in practical batteries. Possible improvements have been reported upon confining SiO₂ into porous carbons or by coating it with carbon.^{4, 5}

In this work, OMC-SiO₂ hybrid compounds have been prepared by the hard template method upon using the mesoporous silica SBA-15 as a template with a coal tar-derived creosote as the carbon precursor. The performance of the materials as the anode for Li-ion batteries was then evaluated.

Materials and Methods

A composite OMC-SiO₂ was obtained by the infiltration of ordered mesoporous silica (SBA-15) with creosote in acidic medium followed by carbonization at 950 °C under inert atmosphere. The composite material was washed with NaOH at different concentrations for 24 h at 40 °C, so that an amount of SiO₂ remaining in the final product could be controlled.

For processing the OMC-SiO₂ hybrid materials were mixed with a water-soluble binder and dispersed in ultra-pure water to form a homogeneous slurry. The weight ratio between the active material and the binder was kept constant (92:8 wt.%). This ink was then sprayed manually on pre-weighed current collectors. The electrochemical measurements were carried out in CR2032 coin cells (Electrolyte: 1 M LiPF₆ in EC:DEC:DMC 1:1:1), where the tested material acted as positive electrode and a Li-metal disk as the negative, reference and counter electrode.

Results and Discussion

As can be seen in Table 1, the insertion of Li⁺ ions at the first cycle was very high, amounting to a capacity of 2090 mA h/g. This value decreased markedly with increasing the amount of residual silica. The same behavior was observed for the first de-insertion. The large difference between the

insertion and de-insertion during the first cycle must be attributed to quite high irreversible losses. The ratio between the reversible and irreversible capacity at the first cycle reached a value of 5.3 for the OMC containing the lowest amounts of silica. However, with increasing amount of residual silica, the relative irreversible losses become smaller. The large decrease in capacity during the first insertion cycle with increasing silica content was attributed to the concomitant decrease in the mesopore volume of the electrodes, *i.e.*, the carbon-binder composite, as noticed in Table 1.

Table 1. Mesopore volume of the electrodes (V_{mp}), first cycle insertion ($Q_{ins(1)}$), de-insertion ($Q_{deins(1)}$) capacities and irreversible capacity/reversible capacity ratio for the different anodes produced from SiO₂-containing OMC.

SiO ₂ (wt.%)	V_{mp} (cm ³ /g)	$Q_{ins(1)}$ (mA h/g)	$Q_{deins(1)}$ (mA h/g)	Q_{irr}/Q_{rev}
1.6	0.64	1928	305	5.32
4.3	0.81	2090	333	5.26
25.3	0.44	1344	245	4.47
40.5	0.27	990	189	4.25
62.7	0.06	558	193	1.89

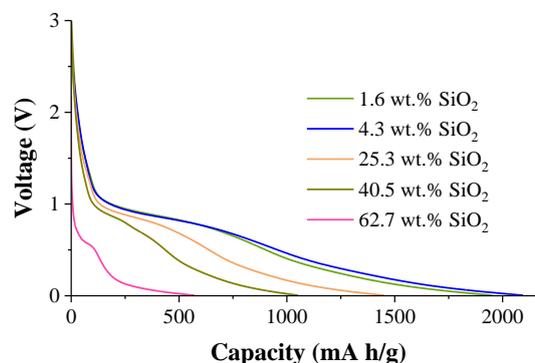


Figure 1. First discharge (insertion) curve of the different (SiO₂-containing) OMC anodes cycled in half-cells.

Figure 1 shows the first discharge curves of the samples. For the lower contents of residual SiO₂, the curves possessed the typical shape of the first Li ion insertion into porous hard carbons. Indeed, a plateau at 0.80 V *vs.* Li⁺/Li corresponding to the formation of the solid electrolyte interphase and a progressive insertion of Li ions into the porous carbon structure was observed. As described above, the insertion capacity decreased with increasing silica content. As a matter of fact, the overall porosity is reduced, limiting the storage capacity of Li ions. Nevertheless, most importantly, a distinct plateau was observed at 0.57 V *vs.* Li⁺/Li for the hybrid containing 62.7 wt.% silica. This potential could correspond to the reduction reactions of lithium ions with SiO₂, resulting in the irreversible formation of Li₄SiO₄ and Li₂O.⁵ As such, Li_xSi_y alloys are formed, which can participate to the charge/discharge processes of the composite anode material.

Conclusions

The insertion capacity of Li ions in hybrid OMC-SiO₂ materials during the first discharge (insertion) cycle was related to the mesopore volume of the electrode composites, with a clear linear dependency. Furthermore, the electrochemical measurements clearly showed the contribution of SiO₂ in the electrochemical reaction at significantly high residual silica contents.

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