

PERFORMANCE OF DIFFERENT COAL-TAR PITCH DERIVED CARBONS IN LI-ION BATTERIES

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Introduction

Secondary batteries are one of the possible alternatives, together with supercapacitors and fuel cells, for supplying energy to new electronic devices. Li-ion batteries are the most promising batteries because of their light weight, high working potential, good cycling behavior and environmental friendly composition [1]. The anodic materials of commercially available Li-ion batteries is made from different types of carbons, but improvements in the performance of the batteries can be expected through the incorporation of new carbon materials that are able to achieve higher capacities and efficiency [2]

However, some technical problems remain unsolved due to the occurrence of an initial irreversible capacity caused by partial electrolyte decomposition during the beginning of the first discharge. The irreversible capacity of the negative electrode provokes that part of the cathode active material is misused, with the consequent economical and technical disadvantages. Fortunately, the solid product deposition formed by electrolyte decomposition on the carbon particle surface renders basically a passivated layer that inhibits the occurrence of this phenomenon for further cycles [3]. The reduction of the initial irreversibility is still one of the main challenges for researchers working in this area. In this sense, the contribution to irreversible capacity of factors such as the nature of the carbon, the carbonization temperature or the role of chemical modifications are evaluated to optimize the performance of these electrode materials[4].

Experimental

A commercial coal tar pitch, supplied by IQN S.A., was treated at 430°C for 4 hours in an inert atmosphere. The resulting treated pitch consisted of a mixture of mesophase spheres (anisotropic phase) in a continuous isotropic phase. Both phases, anisotropic and isotropic, were separated by hot filtration [5] and then submitted to various processes to preserve their microstructure during the carbonisation step. The anisotropic phase was directly submitted to an oxidative stabilisation process in air, which consists in a multi-step programme. Heating was performed at 5° C min⁻¹ to 175° C. After 1h residence time, it was heated at 1° C min⁻¹ to 225 and left at this temperature for another hour. Finally, the temperature was raised to 250° C at 1° C min⁻¹ and maintained for 1 h. The resulting sample, called EST3 was carbonised at different temperatures ranging from 750 to 1000 °C.

The isotropic phase was first subjected to air-blowing (300°C for 10 hour with a flow of air of 40L/h) to increase its softening point, so that it could be oxidatively stabilised. A similar stabilisation programme to that described for the anisotropic phase was used. The final temperature in this case was 270° C. The resulting sample, called IABEST was carbonised at different temperatures ranging from 750 to 1000 °C. To study the influence of the stabilization process part of the air-blown sample was directly carbonized (sample IAB).

The electrochemical experiments were carried out by using two- and three-electrodes Swagelok type lithium cells. Counter and reference electrodes were 9 mm discs of lithium metal and the working electrode consisted of a mixture of 92% active material and 8% PVDF binder coated on a copper foil of the same diameter. A 1 M LiPF₆ (EC: DEC=1:1) electrolyte solution was supported in Whatman glass fiber discs. An Arbin potentiostat/galvanostat multichannel system was used to cycle two electrodes lithium cell at C/50 or C/30 rates for both charge and discharge branches. An Autolab PGSTAT12 system was used for Electrochemical Impedance Spectroscopy (EIS) experiments. For this purpose, a three-electrode lithium cell was successively cycled by passing current between the work electrode (carbon) and the counter electrode (Li). The impedance spectra of the carbon electrode were recorded vs. a Li-reference electrode upon discharging at 0.2 V, allowing the cell to relax in open circuit for at least 5 h to achieve a quasi-equilibrium system. An ac voltage signal of 5 mV was applied from 100 kHz to 1 mHz.

Results and Discussion

The thermal treatment of the coal tar pitch at 430°C for 4 h yielded 70 wt. % of treated pitch, that contained 39 vol. % of mesophase. After hot filtration, about 50 % of each phase, isotropic and anisotropic (mesophase) were obtained. The anisotropic phase (ANI) contained 73 vol. % of mesophase, mainly in the form of spheres, but it also contained an appreciable amount of isotropic phase (27 vol %). Meanwhile, the isotropic phase (ISO) was homogeneous, no anisotropic areas being observed. The anisotropic phase has a higher C/H atomic ratio, higher insoluble content in toluene and NMP than the isotropic phase and higher carbon yield than the isotropic phase, due to the more extensive polymerisation of the mesophase.

Fig. 1 shows the first galvanostatic cycles for both anisotropic (EST3) and isotropic pitch (IAB and IABEST) carbons treated at 750°C. In all cases, a common aspect can be discerned, the first discharge takes place at a higher cell potential and the consumed charge is not completely recovered after the cell charging. This effect is currently assigned to the formation of a passivating film caused by the deposition of the solid products of this reaction on the electrode surface. The porous texture of this film avoids the blockade of the lithium-electrode reaction and further charge/discharge cycles can undergo. For successive cycles, both stabilized samples show a better reproducibility of the discharge branches.

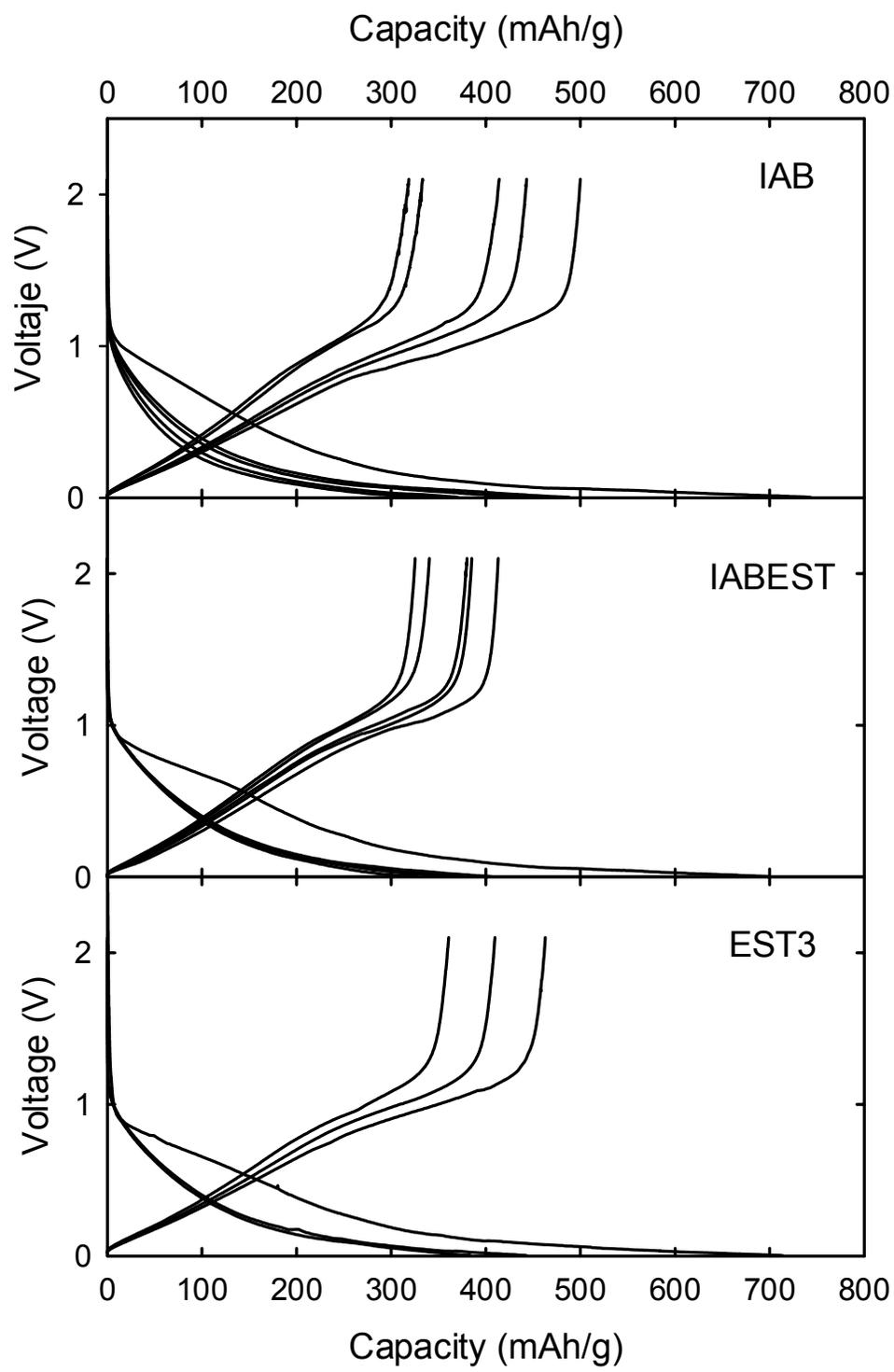


Fig 1: Galvanostatic cycles at C/50 for IAB, IABEST and EST3 samples obtained at 750°C

The stabilization of the samples with air previous to carbonisation at 750°C demonstrated to have beneficial effects on the electrochemical properties probably due to the formation of crosslinks between graphene layers, which stabilize them upon cycling. Moreover, the higher contents of hydrogen and oxygen for IAB sample may indicate the occurrence of surface hydroxyl groups, which hinder the reversibility of the lithium reaction.

A more profound electrochemical study was carried out on the EST3 and IABEST samples by selecting higher carbonisation temperatures. Fig. 2 shows the first cycles for the anisotropic sample EST3 previously carbonised at 700, 800 and 1000°C. For EST3 sample obtained at 700°C, a more extended first discharge was observed which achieved a capacity value close to 750 mAh/g, which rapidly decreases to 370 mAh/g upon the second discharge. A large hysteresis is observed between the discharge and charge branches that has been ascribed to a quasi-reversible binding of lithium to hydrogen located at the edges of the carbon fragments.

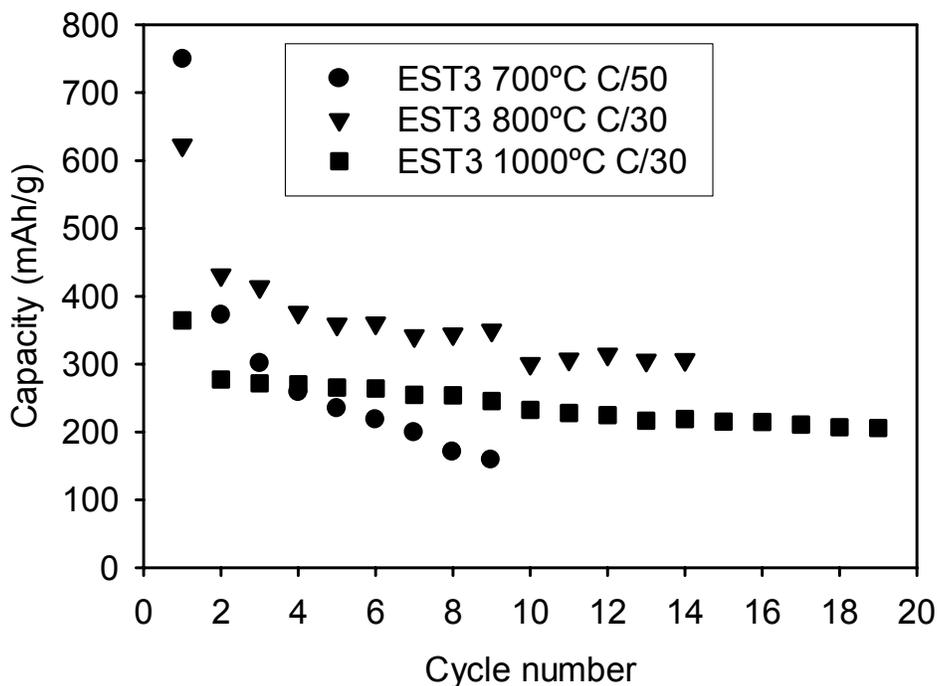


Figure 2: Galvanostatic cycles at C/30 for EST3 at 1000°C and at C/50 for EST3800 and EST3700.

A deeper insight of the influence of surface properties on the electrochemical behaviour of these carbonaceous materials in lithium cells can be deduced from the complex impedance spectra. In this work, the impedance spectra of three selected samples, including both isotropic (IABEST) and anisotropic (EST3) cokes annealed at 750°C and

a 1000°C anisotropic carbon (EST31000), were obtained upon cycling. These spectra were measured on the discharged cell at 0.2 V.

Fig. 3 shows some selected impedance spectra performed as Nyquist plots corresponding to some selected samples partially discharged at 0.2 V. Two depressed semicircles at high and intermediate frequencies, and a straight line in the low frequency extreme, characterize these curves. The first depressed semicircle at the higher frequency interval is ascribed to Li^+ migration through the solid electrolyte interface (SEI). The depression in the semicircle is currently associated to the presence of inhomogeneities in the electrode material such roughness, porosity and/or polycrystalline state, which hinder the frequency dispersion in the interface. A second depressed semicircle at a lower frequency is associated to charge transfer phenomena which during the insertion reaction into the bulk. Finally, a Warburg component describes the response of the system to the Li^+ diffusion through the intercalated carbon [6,7].

The isotropic carbon (IABEST-750°C) is characterized by a higher SEI resistance as compared with anisotropic (EST3-750°C) sample. It could be explained by the differences in average particle distribution and morphology between both samples. Thus, IABEST sample has a lower average particle size $D(0.9) = 156 \mu\text{m}$ (90% of the sample volume corresponds to particles smaller than $156 \mu\text{m}$ in diameter) as compared to EST3 sample for which $D(0.9)$ was equal to $105 \mu\text{m}$. All these data lead to assume a lower specific surface for IABEST in comparison to EST3 sample. For a similar behaviour and consumed charge during the first discharge, it would imply a thicker passivation film in IABEST sample. Moreover, the rougher surface in EST3 sample would involve a more random deposition of the electrolyte decomposition products and consequently a more porous film in which Li^+ ions diffuse with a lesser resistance.

In contrast, the second semicircle, corresponding to the resistance at the insertion charge transfer process which takes place at the passivation film-carbon interface, yields a higher resistance value for EST3-750°C. This result can be associated to the more distorted graphene layers disposition which impedes the lithium reaction with the carbonaceous material. However, its value significantly decreases when carbonisation temperature is increased up to 1000°C (EST3-1000°C). The increase of the carbonisation temperature induces the increase of crystallite sizes, the ordering of the stacked layers, and consequently the resistance to lithium insertion is lowered.

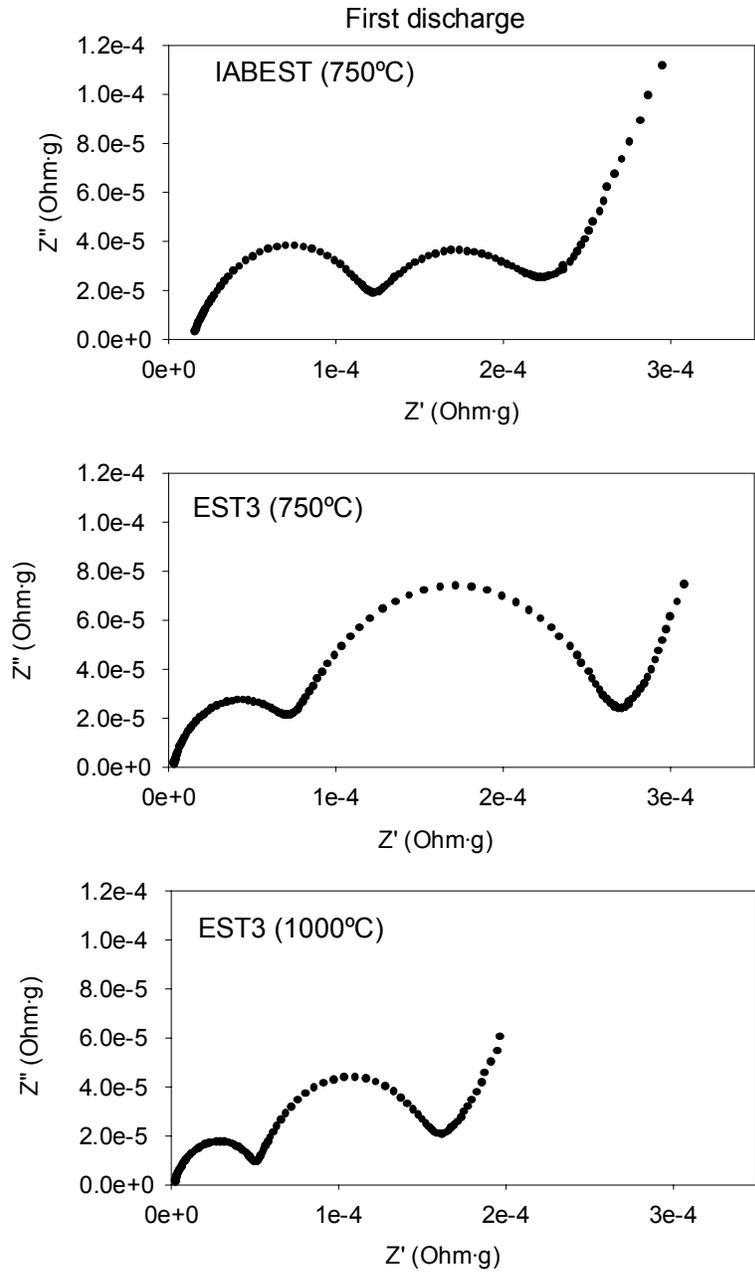


Figure 3: Impedance responses recorded for IABEST and EST3 at 750°C and EST3 at 1000°C.

Conclusions

The different chemical and structural properties of the isotropic phase and mesophase obtained from the same coal tar pitch by hot filtration significantly affect their electrochemical behaviour.

Best capacity values were obtained for the samples that were previously stabilized by oxidation. The increase of the carbonisation temperature over 800°C involves a better capacity retention

The EIS have proved to be an interesting tool for researching the surface phenomena that could affect to the electrode performance. Thus, the overall resistance on the carbon surface is more affected by charge transfer phenomena in anisotropic phase derived materials while the passivation film is the greater component for the isotropic phase based materials after the first discharge.

References

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