Electrical and Electrochemical Characterization of Petrol Cokes for Lithium-Ion Cells

C. DEL RÍO, M. C. OJEDA, J. L. ACOSTA

Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva, 3 28006 Madrid, Spain

ABSTRACT: Several cokes and graphites have been electrically and electrochemically characterized. The process of electrochemical lithium ion insertion into these materials has been analyzed for the purpose of assessing their performance as electrodes in advanced batteries and as potential candidates to substitute for lithium metal. The results obtained prove the process of electrochemical lithium ion insertion into cokes and graphites to be strongly influenced both by the ordered structure of the starting material and by the nature of the anion of the lithium salt, which is used as electrolyte. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1003–1008, 1999

Key words: lithium batteries; carbon electrodes; electrochemistry; impedance spectroscopy; cyclic voltametry

INTRODUCTION

In the industrialized countries the automobile has been subject to new developments that have stimulated research on advanced batteries, both for high temperatures (Na/S, Li/Fe-S$_2$, etc.) and ambient temperature (Li/polymer, Li-ion, metal hydride/Ni OOH, etc.).

Lithium metal distinguishes itself as the most attractive negative electrode for rechargeable lithium batteries,[1–3] due to its high specific power (3862 mAh/g) and high voltage ($\simeq$3 V) when used in devices not containing any aqueous electrolytes. From a technological and environmental point of view, however, two problems had to be coped with, which proved difficult to solve: the first of these related to the limited number of discharge–charge cycles, and the second referred to safety problems. This was the reason why alternative materials were being developed during the 90s that would avoid the presence of lithium metal as the negative electrode. This led to the idea of replacing lithium by carbon compounds with a high ion-insertion potential. The feasibility of these developments was readily established by the industrial manufacture of some battery prototypes based on lithium ions (Sony Corporation), as well as by the massive involvement of academic and industrial research in this field.

One of the objectives with a major interest on the development of lithium ion batteries is the production of carbon-based materials with a high lithium-insertion and storing potential. The theoretical lithium ion insertion power of graphite is 372 mAh/g, whereas values above 600 mAh/g have been reported exclusively for amorphous carbons.[4–7] On these lines, this research focusses on the analysis of a series of industrially obtained cokes, from an electrical and electrochemical point of view, in order to assess their performance as negative electrodes in advanced lithium ion batteries. The results obtained are compared to those recorded for commercial graphites.

EXPERIMENTAL

Four cokes were used, supplied by Repsol Inc. in powder form: Coke 1 (regular), Coke 2 (recarburant), Coke 3 (intermediate), and Coke 4 (combus-

tion), as well as three graphites also used in powder form: Graphite 1 (recarburant), from Repsol Inc., Graphite 2 (KS-44) from Lonza, and Graphite 3 from Kishida Chem. The polymer binder used was polyvinylidenefluoride (PVDF) supplied by Solvay (Solef 6010).

Three different lithium salts were employed in electrolyte preparation: lithium triflate ($LiCF_3SO_3$), lithiumphosphate hexafluoride ($LiPF_6$), both from Aldrich Inc., and lithium trifluoromethanesulfonimide ($LiN(CF_3SO_2)_2$), supplied by the 3M Company. The solvent used was a blend of dimethyl carbonate (DMC) and ethyl carbonate (EC), the DMC/EC ratio being 2 : 1. Prior to electrode preparation the cokes and graphites were vacuum dried at 120°C for 10 h. By the same token and prior to electrolyte preparation, the lithium salts were vacuum dried at room temperature for 10 h and then stored in Argon atmosphere in a glove box. The solvents were stored in a glove box on 4 Å molecular sieves, ready for use.

The electrodes were obtained by means of the following procedure: 10% PVDF was dissolved in dimethyl sulfoxide (DMSO), and the carbon was dispersed in the resulting solution. The dispersion was applied to stainless steel pellets, diameter 1.2 cm and thickness 0.5 mm, the solvent being subsequently evaporated in an oven at 100°C for 24 h, after which time the drying process was complemented by an additional 10 h of vacuum drying at 120°C.

The three electrolytes used were prepared soaking a glass microfibre filter (Whatman GMF 150) in an 1M solution of the respective salts in a DMC/EC blend, ratio 2 : 1.

The electrical characterization was conducted by means of complex impedance spectroscopy using cells of a configuration steel/electrode-carbon/steel connected to a Hewlett Packard impedance analyzer, model HP 4192A LF. Impedance was measured as a function of temperature on an Oxford Instruments cryostat, model ITC4.

For electrochemical lithium insertion in the carbon electrode a MacPile II galvanostate was used from Bio Logic Science Instruments. The configuration of the measuring cell was as follows: Li/electrolyte/carbon electrode. In all cases the weight of the active material was comprised in the range of 5 to 25 mg.

Electrochemical characterization was conducted by means of cyclic voltametry analysis at room temperature on a Copenhagen Radiometer, model IMT 101, varying the voltage at a rate of 20 mV s^{-1} over a range of -1 to 5 V.
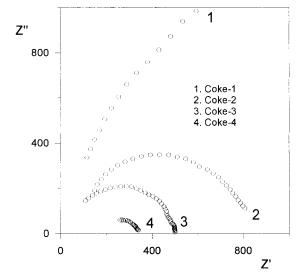

Figure 1   Complex impedance arcs of cokes at 298 K.

RESULTS AND DISCUSSION

Electrical Characterization

Impedance measurements have been widely used to characterize electrode systems, and have been highly advanced in various field of materials science associated with electrochemistry. Impedance measurements especially become one of the most important electrical and electrochemical method for studying materials for advanced lithium batteries such as carbon materials, lithium–ion-conducting solid electrolytes including solid polymer electrolytes, and so forth. Analysis of experimental results $Z(\omega)$ vs. ω over a wide range of frequencies is normally done using an equivalent circuit consisting of resistors, capacitors, inductors, and dispersion elements. When an appropriate equivalent circuit is used to fit impedance data, parameters obtained may help characterize materials or electrode systems.

Following the methodology indicated, the carbonaceous starting materials were electrically characterized at room temperature, the respective data being shown in Figures 1 and 2. Sample conductivity was determined from the respective arcs obtained, as compiled in Table I. Figures 1 and 2 show all materials to present a semicircle on the impedance plane whose centre is not situated on the abscise axis and that describes the electronic conductive behavior inside the material. In terms of their σ value, all the experimental graphites present an electrical borderline behavior between insulating and semiconductor
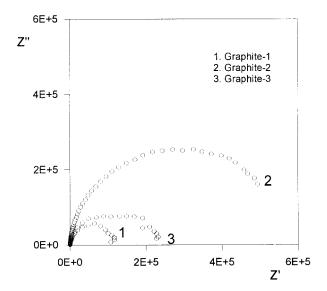
Figure 2   Complex impedance arcs of graphites at 298 K.

Figure 3   Log σ as a function of temperature for Coke 2.

materials, whereas the cokes are straightforward semiconductors (except Coke 1). To test the semiconductor character of these cokes the effect of temperature on conductivity was assessed as shown in Figure 3 for Coke 2. The decrease of conductivity with increasing temperature is a typical feature of semiconductors, and was recorded for all coke samples.

Apart from conductivity, all the materials tested have a similar equivalent circuit, consisting of a resistance in parallel with a condenser.

Electrochemical Lithium Insertion in Graphites and Cokes

The lithium insertion properties of the four petroleum cokes used were compared to those of three graphites. Each sample was tested with three different electrolytes to determine the contribution of the anion, which accompanies the lithium

Table I σ **Values of Different Samples at 298 K**

Sample	$\sigma(S \cdot cm^{-1})$
Graphite 1	$1.607 \cdot 10^{-7}$
Graphite 2	$1.078 \cdot 10^{-7}$
Graphite 3	$5.377 \cdot 10^{-8}$
Coke 1	$2.260 \cdot 10^{-8}$
Coke 2	$1.275 \cdot 10^{-5}$
Coke 3	$5.667 \cdot 10^{-5}$
Coke 4	$1.204 \cdot 10^{-4}$

ion, to the insertion properties. Figure 4 shows the galvanostatic discharge–charge plots up to a maximum of 20 cycles for each coke, the electrolytes being lithium triflate (A), lithiumphosphate hexafluoride (B), and lithium trifluoromethane sulfonimide (C). Similarly, Figure 5 shows the test results using the three graphites as host materials. As generally known, the lithium insertion properties in carbonaceous materials basically depend on the carbon chain structure. Graphites, however, are known to have a crystalline structure; its basic building block is a planar sheet of carbon atoms arranged in a honeycomb and stacked in a registered fashion[8] (polymorphes of graphite). The situation is even more complex for carbon in general: cokes, petroleum cokes, carbon blacks, carbon fibers, mesocarbons, microspheres, etc.; most of these have disordered structures where the size of the crystallites is small, and where there is large probability that adjacent carbon layers are randomly stacked. Random stacking means that the layers are basically parallel, but random shifts or rotations are found between adjacents layers; this type of disorder is called turbostratic disorder[9] and disordered carbons are soft carbons where turbostratic disorder is easily removed by heating above 2200°C and hard carbons for which it is difficult to remove the turbostratic disorder at any temperature.
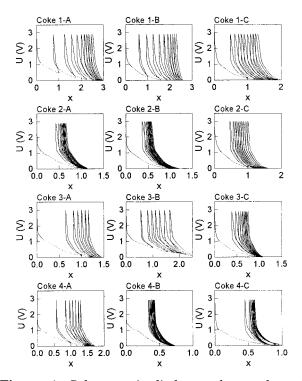
Figure 4 Galvanostatic discharge–charge plots of cokes using different electrolytes: (A) $1M$ (LiCF$_3$SO$_3$) in DMC : EC 2 : 1, (B) $1M$ (LiN(CF$_3$SO$_2$)$_2$) in DMC : EC 2 : 1 and (C) $1M$ (LiPF$_6$) in DMC : EC 2 : 1.

The first global difference found in the lithium ion insertion properties in the cokes and graphites tested (Figs. 4 and 5) and attributable to structural factors, refers to the voltage at the onset of the insertion process. Whereas reversible lithium ion insertion sets in around 1.2 V for the cokes, this process is initiated at 0.3 V in the graphites. By the same token, the profile of the voltage plot in the coke cells (Fig. 4) is slanted, while that of the graphite cells is flat. Dahn[10] explains the large slanted slope observed for cokes by means of theoretical models. As a consequence of the disorder in cokes it expects the site energy to vary from site to site. If the site energy variation is large enough, lithium atoms will reside in the sites of lowest energy, regardless of their position, and will not cluster together into neighboring sites to form islands as they do in the absence of a site energy variation; therefore, disorder in the host should suppress the formation of staged phases. So, the spacing between the carbon sheets expands as lithium is added but the disorder in the cokes is unaffected by the intercalation; when the lithium is removed the host layers revert to their original spacing.

The remaining differences recorded in the lithium ion insertion processes in cokes and graphites are basically due to the different polymorphs within each family as well as to the different lithium salt anions used as electrolytes in the insertion reaction. Considering the insertion processes in the cokes, whose results are shown in Figure 4, a loss in potential can be observed in all cases during the first discharge cycle, attributable to a minor decomposition reaction of the electrolyte and the generation of an interface on the coke surface, right at the interface with the electrolyte. In addition, and as a function of the nature of the anion of the respective salt used as an electrolyte, both the insertion level (x) during 20 discharge–charge cycles and the potential prove to be affected. For instance, in Coke 2 good reversibility is observed throughout the 20 test cycles, except when electrolyte C is used. In contrast, for Coke 4 reversibility is good with electrolytes B and C but bad with A, although the insertion level reached with any of these electrolytes is always lower than for coke 2. Reversibility is bad in Cokes 1 and 3 for any of the three electrolytes.

The insertion processes in the experimental graphites (Fig. 5) also show differences among themselves. One of the characteristics of graphites that makes them good candidates to perform as battery electrodes is that they insert lithium ions at very low voltage (0.3 V). Nevertheless,
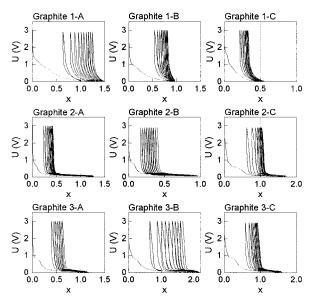

Figure 5 Galvanostatic discharge–charge plots of graphites using different electrolytes: (A) $1M$ (LiCF$_3$SO$_3$) in DMC : EC 2 : 1, (B) $1M$ (LiN(CF$_3$SO$_2$)$_2$) in DMC : EC 2 : 1 and (C) $1M$ (LiPF$_6$) in DMC : EC 2 : 1.
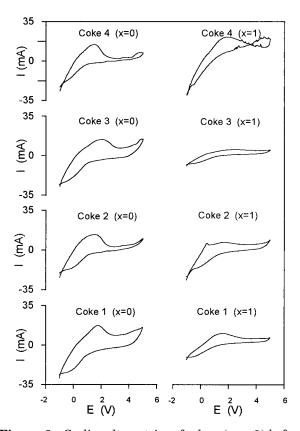
Figure 6 Cyclic voltametries of cokes: ($x = 0$) before first discharge cycle and ($x = 1$) after first discharge cycle.

Graphite 1, irrespective of the salt used, initiates the insertion reaction at a voltage similar to that of cokes, with considerable losses in potential overall the 20 test cycles. This behavior deviates from the general pattern of graphites, and can be seen in Figure 5 as contrasting to those of Graphites 2 and 3. In all cases and comparable to the coke data, a noticeable loss in potential is observed as of the second cycle, which is due to the same phenomena occurring in cokes, i.e., electrolyte decomposition and metal deposition at the electrode–electrolyte interface. Lithium insertion reversibility is good in Graphites 2 and 3, except when electrolyte C is used in Graphite 3. In all cases, excellent insertion levels are achieved.

Electrochemical characterization eventually comprised the analysis of the cyclic voltametries of all the carbons used, which supplies information regarding electrochemical stability and the reversibility of the oxidation-reduction reactions that take place in the voltage range tested. Figures 6 and 7 show the voltamograms prior to the insertion reaction ($x = 0$) and after the first

discharge cycle ($x = 1$) of the experimental samples, both for coke and graphite. Only the second cycle is plotted, as it is representative of the voltamograms of all subsequent ones.

In the graphite voltametries (Fig. 6) it can be observed that the electrochemical stability windows are reduced, as a general rule, after the first discharge cycle especially in Graphites 2 and 3, which reach stability approximately between 1 and 4 V: for $x = 0$ at 2 V, and for $x = 1$ at 4 V. Graphite 1 is electrochemically stable between approximately 3 and 4 V, irrespective of the insertion process.

Prior to the first discharge cycle ($x = 0$), the cokes (Fig. 7) possess smaller electrochemical stability windows than the graphites. After lithium ion insertion ($x = 1$) there appear a variety of behaviors: Cokes 1 and 3 improve their stability, Coke 2 shows the same behavior before and after the insertion, and Coke 4 ceases to be stable as of 3 V.

CONCLUSIONS

The lithium ion insertion process in cokes and graphites is governed both by the structure of the host materials and the characteristics of the anion of the salt serving as the electrolyte. Within
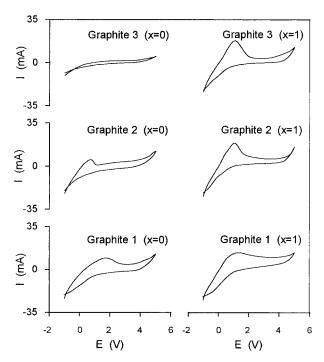

Figure 7 Cyclic voltametries of graphites: ($x = 0$) before first discharge cycle and ($x = 1$) after first discharge cycle.

the coke series tested, Cokes 2 and 4 clearly present better insertion and reversibility properties than Cokes 1 and 3—especially Coke 2, when electrolyte B is used. The lithium ion insertion processes in Graphites 2 and 3 are especially favored when utilizing electrolytes A and C, giving rise to large insertion areas and excellent reversibility, in contrast to Graphite 1, whose behavior approaches that of cokes regarding the insertion triggering voltage. It deviates from cokes, however, even if it presents good reversibility with electrolytes B and C, as to the insertion level, which remains consistently low.

REFERENCES

1. Subbarao, S.; Koch, V. R.; Owens, B. B.; Smyrl, W. H. Rechargeable Lithium Batteries; The Electrochemical Society, Inc., Proceedings; 1990, Vol. 90-5.
2. Scrosati, B. Applications of Electroactive Polymers; Chapman and Hall: New York, 1993.
3. Pistoia, G. Lithium Batteries; Industrial Chemistry Library, Elsevier: New York, 1994, Vol. 5.
4. Mabuchi, A.; Tokomitsu, K.; Fukimoto, H.; Kasuh, T. J Electrochem Soc 1995, 142, 1041.
5. Alamgir, M.; Zuo, Q.; Abraham, K. J Electrochem Soc 1994, 141, L143.
6. Sato, K.; Noguchi, M.; Demachi, A.; Oki, N.; Endo, M. Science 1994, 264, 556.
7. Tatsumi, K.; Zaghib, K.; Abe, H.; Oshaki, T.; Higuchi, H.; Sawada, Y. 185th Meeting of the Electrochemical Society; The Electrochemical Society: Miami, October 9–14, 1994, Abstract #142.
8. Bernal, J. D. Proc R Soc 1924, A106, 749.
9. Frankin, R. F. Proc R Soc 1951, A209, 196.
10. Dahn, J. R.; Fong, R.; Spoon, M. J. Phys Rev 1990, B42, 6424.