From Rome to Como: 20 years of active research on carbon-based electrodes for lithium batteries at INP-Grenoble

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Abstract

This paper reviews the main areas of research performed at different Laboratories of the Institut National Polytechnique de Grenoble (INPG) over the past 20 years, specifically on cabonaceous materials for electrode applications in lithium batteries. The most significant event was the discovery in the early 1980s of reversible lithium intercalation into graphite in polymer electrolytes, which led to the use of this material in today's lithium-ion batteries. Important work was also carried out on positive electrode for primary and secondary batteries, especially graphite oxide and graphite fluoride. Most of these results were presented at the 10 IMLB series Symposia, which started in Rome in 1982 and were back to Como, Italy, in 2000. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Graphite is one of the allotropic forms of carbon characterized by a 3D ordered structure consisting of carbon flat layers (called graphenes) arranged in a regular stacking sequence along the *c*-axis. In each graphene, the carbon atoms occupy the corner of a regular hexagon, each hexagon sharing one edge with six neighboring ones. A honeycomb like planar structure is formed. The in-plane C–C distance is of the order of 1.41 Å, and the out-of-plane inter-graphene distance is of the order of 3.35 Å. There is a very strong anisotropy in the C–C binding energy between in the in-plane and the out-of-plane directions. The former is strongly covalent and the later is of the much weaker van der Waals type. Such a structure is at the origin of the various anisotropic physical and chemical properties, especially those related to the electron, heat and mass transport.

Graphite intercalation compounds (GICs) are formed because of the possibility offered by the graphenes to easily expand in the *c*-direction allowing chemical species to diffuse between them and under specific conditions to form new crystal phases. Among the most characteristic features of GICs is stage formation that is two adjacent intercalate layers are regularly separated by a constant number of graphenes. The later is called the stage number. By increasing the stage number, one increases the 2D character of the GIC. This feature has being widely exploited in the physical properties, especially in magnetic ones.

In the field of electrode materials for lithium batteries, graphite and GICs offer a wide range of exciting features that made it possible to use them in practical applications. Among these, some are particularly worth mentioning here.

- Graphite is an electronically amphoteric material in the sense that it accommodates both electron donors and acceptors. Alkali metal GICs are the most characteristic ones for donor type and transition metal halides or nitrates or acid-based GICs are among the classical acceptor ones. A charge transfer between the intercalate and the graphene has been showed to take place. It leads to a partial negative charge on the carbon for the donor type and a positive one for the acceptor type. Such transfer might be translated, respectively, to a reduction and to an oxidation of the graphene. The electron energy level, especially the Fermi level is increased or decreased, therefore, the electrode Nernst potential will, respectively, be decreased or increased. Hence, GICs with donors are likely to be used as negative electrodes (anode during discharge) and those with acceptors as a positive ones (or cathodes). As a matter of fact, the Li_xC_6 electrode works around

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100–200 mV versus Li and $C_{24}BF_4$ electrode works in the 4.5 V versus Li potential range.

- GICs offer a wide range of non-stoichiometry, in particular very dense structures can be formed with a high intercalate/carbon molecular ratio. Examples of these can be found with super-dense alkali metal phases such as LiC_2 and with graphite fluoride $(CF)_n$ structures. Such a feature is of importance when determining the electrode specific capacity. Moving from high intercalate to low intercalate density phases would generate higher capacity as the electron stored or released is bound to the intercalated and de-intercalated ion. As a matter of fact, LiC_2 would theoretically generate up to 1116 mAh/C g and $(CF)_n$ up to 864 mAh/$(CF)_n$ g.

- Electron donor or acceptor types GICs have a high electrical conductivity, which may match that of some metals such Al. This allows a fast charge transfer during the electrochemical reaction. In addition, the easy expansion along the *c*-axis together with a lower stacking defect concentration makes the diffusion within the graphenes faster. Hence, the electrode polarization under high rates will be reduced. Covalent type GICs such as $(CF)_n$ and graphite oxide (of ideal composition C_4OOH) are known to be rather insulating materials. However, their chemical reduction generates pure carbon which then enhances the electrode conductivity as they discharge.

- Although ionic type intercalated species may partly dissolve in organic liquid electrolytes and/or form solvent co-intercalated compounds, a stabilizing mechanism such as the passivation that leads to the solid electrolyte interface (SEI) formation in the case of Li_xC_6 eventually take place and makes it possible to operate the electrode with minor risks of self-discharge and/or solvent co-intercalation. Obviously such protection is temperature-dependent. On the other hand, covalent type GICs may be considered as insoluble in the electrolytes even at higher temperature.

- The lithium intercalation is reversible in some cases such as in the Li_xC_6 negative electrode. This is also the case for some anions such as ClO_4^-, PF_6^- and BF_4^-, which were proposed for use as reversible positives. However, the volume expansion in the latter may reduce such possibility.

At the INPG, we have been involved in studies of GICs for electrode application in lithium batteries from the mid- and late-1970s starting with the pioneer work of Touzain and Armand [1] who showed the potential use of transition metals chlorides compounds as cathode materials. This was followed up by a more systematic study of other materials such as graphite–lithium for the anode and graphite oxide for the cathode. It was in the early 1980s that we showed for the first time that lithium could be reversibly intercalated into graphite using an electrochemical cell with a polymer electrolyte [2]. This result was presented during the first IMLB held in Rome in May 1982 and published in

the meeting proceedings [3]. Several months later, Bell Labs were awarded a US patent on the use of lithiated graphite in liquid electrolyte [4]. It was only at the end of the 1980s and beginning of the 1990s that the research activity in this area was intensified, especially in Japan. This led Sony, to be followed by other companies, to introduce the lithium-ion battery in the market with the success known today.

In Section 2, I summarize the main research area covered since then at the successive Laboratories of the INPG, in association with the CNRS.

2. The lithium–carbon "anode"

After the Rome meeting, we focused on the kinetics of the lithium–graphite electrode compared with two other light alkali metals: Na and K [5]. By using polymer electrolyte-based cells and intermittent galvanostatic techniques, we measured the chemical diffusion coefficient and found them in the increasing sequence of $K(\approx 10^{-7} \text{ cm}^2 \text{ s}^{-1}) > Li(\approx 10^{-8} \text{ cm}^2 \text{ s}^{-1}) > Na(\approx 10^{-11} \text{ cm}^2 \text{ s}^{-1})$. This was on the same order as the affinity of graphite with the corresponding alkali metal.

Although the activity on the negative electrode work slowed by the end of the 1980s, we maintained a close watch on what was occurring in the field until the beginning of the 1990s with the Sony announcement. Then different aspects of the lithium–carbon electrode behavior were investigated. This comprises the following:

- *Reducing the irreversible capacity*: the lost capacity during the early cycles on the negative electrode side is generally associated with the passivation phenomenon that leads to the SEI formation. We found that a preliminary chemical lithiation of materials such as coke or graphite powders and carbon fibers reduces dramatically the initial capacity losses [6]. The lithiation was carried out either in liquid solutions such as butyl-lithium in hexane or lithium naphtalenide in THF or in molten metallic lithium around 220°C.

- *Increasing the reversible capacity*: we found that some semi-cokes (also called "green carbon") heat treated below 500°C show a huge reversible capacity beyond 1600 mAh/g when used in dry polymer electrolytes at around 100°C. The capacity was found to vary linearly with the operating temperature. By increasing the semi-cokes heat treatment temperature, the capacity falls below 700 mAh/g, but concomitantly, the irreversible capacity decreased too [7]. To cope with the excess capacity, we proposed a model of lithium multilayers on the external basal C-layers. The later being of a few nanometers in the diameter and of up to three stacking layers. We also showed the effect of pressure on the reversible capacity of these materials and found up to 2200 mAh/g under ca. 100 bars. The additional capacity was related to the enhanced electrode wetting with the polymer electrolyte.

- *Reversible versus irreversible capacity*: based on a statistical study using different graphite materials, we established a simple relationship between the amount of lithium stored between the graphenes and that consumed on the surface to form the SEI (respectively in relation with the reversible and irreversible capacities). The dependence was found to be close to linear. We showed that graphite with lower irreversible capacity is more likely to yield a higher reversible one. This was related to an activation energy effect in relation with the bulk and surface structures [8]. As "easily" intercalated graphite require less energy to access to the graphene (higher crystallinity, lower surface defects), the "stay time" in the absorbed form of deposited lithium metal on the surface is shorter. This makes it less likely react with the electrolyte. As a result, the amount of SEI is lower and consequently, so is the lithium diffusion resistance. The alkali metal would then be intercalated in larger amounts under the same current density.
- *Characterization of the passivation layer (SEI)*: we formed the SEI by a chemical route by reacting pre-lithiated graphitized fiber [9] or a highly oriented pyrolytic graphite (HOPG) [10] of LiC_6 composition with 1 M $LiPF_6$ in EC solution. Lithium then de-intercalates from LiC_6 and reacts with the electrolyte in a similar way than during the electrochemical reduction. The differences, however, stand in the larger amounts of SEI formed by the chemical route that allows a more accurate characterization of its chemical and physical properties. FTIR spectrometry made it possible for us to show for the first time the polymer character of the SEI. In particular, we could assign absorption lines to the polyethylene oxide and to some polycarbonates as a result of the EC decomposition and/or polymerization. This polymer part of the SEI was shown later to dissolve in the liquid electrolyte at higher temperature [11,12]. By coupling AFM and XPS, we showed the morphologies of the SEI at different scales (from 1 micron to 3 nanometers) [10] and analyzed its composition. After cleaving the HOPG-based sample, we showed that the SEI not only formed on the geometrical external surface of the graphite but also grew between the crystallites, a few 10 micron deeper from the external surface. We also established a hierarchy in the reaction with the electrolyte that is LiF is first formed probably as result of HF impurity or PF_6^- reduction to poorer fluorine containing phosphorus. Then the EC is reduced to form gases and more likely the polymer and the Li-alkyl-carbonates.
- *Stability versus the electrolytes*: in an attempt to understand the role of each component of the electrolyte among EC, PC, DMC, DEC and DME in the SEI formation, we reacted HOPG-based LiC_6 with a $LiPF_6$ solution of these solvent and with their mixture with EC [13]. We found that except for the EC case, all the other single solvent-based electrolytes tend more or less to co-intercalate between the graphenes. The most spectacular result

was observed with PC, which led to a huge expansion and total disintegration of the LiC_6 specimen (exfoliation). The other significant finding of this study was that when EC is used in association with any other of the above cited solvents, no (or a very limited in the case of PC) co-intercalation is observed. Therefore, EC plays an important role in the SEI formation and stabilization. Such a stability, however, is only kinetic in nature, co-intercalation takes place at much higher temperature as result of the SEI partial dissolution.

- *Mechanism of self-discharge*: the thermal storage of Li/organic electrolyte/Li_xC_6 half-cells was carried out in the lithiated [14] and the de-lithiated states [15] of graphite after several charge and discharge cycles. The effect on the electrode capacity and the interfacial properties was investigated by galvanostatic cycling and by impedance measurements (EIS). Two types of capacity losses were found depending on the storage temperature and duration, a reversible and an irreversible one. The former was tentatively related to either the very small electronic conductivity of the electrolyte or more likely to the formation of a metastable electron–ion–molecule complex adsorbed on the graphene edges. The lithium used in this complex accounts for the capacity loss. However, the complex would re-dissociate to its elements as the electrode potential is driven to more cathodic polarization during the re-lithiation step. Such mechanism allows the adsorbed lithium ion to re-intercalate and be used in the following de-lithiation. In this case the capacity loss is reversible. With increased temperature, the electron–ion–molecule complex recombines to form new compounds as the result of the solvent(s) or the lithium salt anion reduction (total electron transfer). Such a reaction is irreversible in nature. The comparison of the interfacial properties versus time evolution in lithiated and de-lithiated electrodes carried out by means of EIS and XRD led us to the conclusion that the SIE undergoes some chemical transformations during the storage. The inorganic part (composed for the most of LiF and LiO_x) tends to increase in thickness while the organic part dissolves in the electrolyte [14]. Since the inorganic part is much less ionically conductive, the electrode becomes gradually isolated from both electrons and ions, which then leads to its end of life.
- *Super-dense phases*: Li_xC_2 GIC can be obtained under high pressure–high temperature conditions. We performed the first electrochemical measurement on these materials in collaboration with the Moscow University and Nancy University groups. The most striking result was the observation of a negative OCV versus Li of the Li_xC_2 electrode at the ambient temperature. This is to the author knowledge the only example of such unusual result. However, due to the irreversible decomposition of Li_xC_2 to $LiC_6 + Li$ at the ambient temperature and pressure, Li_xC_2 phase could not be restored after full

Table 1
Summary of the presentations made by the author (except for *) during the 10 successive IMLBs

IMLB #	City	Date	Main topics covered			Comments	References
			Li_xC_6	C_4OOH_x	CF_x		
1	Rome	27–29 April 1982	X			First public announcement of the lithium–graphite anode	Proceedings' abstract #23 and [2]
2	Paris	25–27 April 1984		X		Graphite oxide	[16]
3	Kyoto*	27–30 May 1986		X		Improved graphite oxide	Proceedings' abstract # SW-12
4	Vancouver	24–27 May 1988			X	Semi-ionic CF_x	Proceedings' abstract #14
5	Beijing	27 May–1 June 1988			X	Li/polymer/CF_x and GICs with metal fluorides	Proceedings' abstract #PB 26 and 27
6	Munster	10–15 May 1992	X		X	Structure and electrochemistry of Li_xC_6 GICs with metal oxides fluorides	Proceedings' abstract # MON5 and III-B19
7	Boston	15–20 May 1994	X		X	Electrodes in polymer electrolytes	[7]
8	Nagoya	16–21 June 1996	X			EIS measurements High capacity carbon and SEI	Proceedings' abstract # THU-01, 1-A-17–19
9	Edinburgh	12–17 July 1998	X		X	Passivation and SEI characterization	Posters session
10	Como	28 May –2 June 2000	X			EIS-ageing	Paper #77

de- and re-lithiation cycle. Therefore, the cycle capacity of Li_xC_2 did not exceed that of LiC_6.

3. Covalent type GICs

Graphite fluoride $((CF_x)_n)$ and graphite oxide (C_4OOH_x) are the best known examples of covalent type GICs. They are formed under highly oxidizing conditions such as under strong anodic polarization (as in fluorine molten salts cells or in strong acids electrolyte solutions) or by chemical oxidation under fluorine at high temperature for $(CF_x)_n$ or with a mixture of strong acid and an oxidizing agent (i.e. $HNO_3 + KClO_3$ or $H_2SO_4 + KMnO_4$) for C_4OOH_x. The resulting compounds are characterized by a strong C–F and C–O covalent bonding, respectively. This induces a change in the carbon hybridization from the planar sp^2 to the tetrahedral sp^3. $(CF_x)_n$ and C_4OOH_x show excellent cathode materials properties for primary battery applications. In particular, they exhibit the highest specific capacity (over 860 and 990 mAh/g, respectively). In addition they discharge at high voltage (2.6–2.8 V versus Li) and show a good stability versus the electrolyte. $(CF_x)_n$ has been used in practical lithium primary batteries since the mid-1970s.

Our contribution in this field mainly concerned the clarification of the relation between the synthesis conditions, the physical and chemical characteristics and the electrochemical properties. We improved the oxygen content of the C_4OOH_x by using a high specific surface area and fine graphite powder as starting material and by applying a second oxidation [16]. As consequence, practical capacity as high as 800 mAh/g was achieved.

Regarding the graphite fluoride, in collaboration with the University of Clermont-Ferrand in France, we sat in new route to form $(CF_x)_n$ compounds at temperatures as low as the ambient [17]. The resulting material is semi-ionic (or semi-covalent) in nature with preserved sp^2 carbon hybridization. As consequence, the electrode reduction overpotential is much lower than in the purely covalent form. The achieved practical capacity was beyond 700 mAh/g and the average discharge voltage close to 3 V under C/20 current rate. The new material sustained up to $4C$ rate yielding an energy density over 1200 Wh/kg of $(CF_x)_n$ [18,19]. Such outstanding behavior was related to the higher charge mobility (ion and electron) due to the preserved graphenes planarity. This was confirmed by a comparative EIS study of covalent and semi-covalent graphite fluorides.

Currently, a project on the semi-covalent graphite fluoride is in progress supported by the ANVAR (French National Agency for the Vaporization of Research).

4. Conclusion

What characterizes the most our research activity on GICs for lithium batteries is the over 20 years uninterrupted effort to investigate different candidates for anode and cathode applications. We performed the pioneering work on lithiated graphite and on the SEI characterization. We continuously direct our efforts toward better understanding of the basic mechanisms that govern this electrode operation, such as the passivation and the lithium storage. We also extended the studies to other alkali metals GICs and other types or carbonaceous materials including fullerenes. Super-dense phases such as Li_xC_2 were also investigated. New methodologies were introduced to study the step-by-step lithium intercalation such as very slow scan voltammetry [20] and more recently three and four electrode coin cells for EIS studies.

Regarding the cathode materials, we have developed new syntheses routes for graphite oxide and fluoride, but also investigated the high voltage anion intercalated graphite [21] together with those formed with transition metals chlorides [22]. This generated over 60 published papers and over 10 patent applications. Among them, those presented during the 10 IMLBs are summarized in Table 1.

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