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Review

Electrochemistry of graphite intercalation compounds

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Abstract

This review starts with a brief historic outline of the developments in graphite intercalation compounds (GICs) and their predominant application in the field of electrochemical energy systems. The structural outline of ideal GICs and the real irreversible transformations during intercalation/de-intercalation cycles is considered in detail. A general outline of the chemical, electrochemical and the newly introduced photochemical methods for the preparation of GICs is then provided. After a brief discussion of the wide ranging surface analytical tools employed in the characterization of GICs, selected methods of characterization widely employed in the electrochemical context are described with suitable examples. A fairly detailed account of the electrochemistry of donor, acceptor GICs and graphite fluorides which essentially transform into GICs during discharge is also given. Finally, an outline of battery systems that employ at least one intercalated electrode is provided. The scope for further research and development in this area is also indicated. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Graphite electrodes; Intercalation; Battery systems; Lithium-ion battery

1. Introduction

Among the modified graphite materials [1], graphite intercalation compounds (GICs) have certainly attracted the attention of theoretical physicists, chemists, and industrialists. A recent survey [2] indicates that H₂SO₄-based GICs were reported in literature as early as 1841. Table 1 indicates the continuous efforts, successes and developments in this area during the past 15 decades. The improved electrical, electronic and catalytic properties of these graphite intercalation systems has led to a variety of new applications in electrical, electrochemical and chemical industries over the decades. With the discovery of high-temperature, mixed oxide super-conductors in the late 1980s, however, there has been a noticeable shift in emphasis in the research of GICs from attempts to improve the electronic conductivity towards efforts to find newer industrial applications and improved efficiency in the existing industrial application areas [3,4]. Quite naturally, there is considerable primary and secondary literature [5–15] [16–22] in this growing field. Some specific reviews outlining developments in individual nations such as France [23] and Japan [24] have also appeared. Even specific areas

of graphite intercalation compounds (GICs) such as ternary graphite systems have been reviewed in detail [25,26]. Recently, there has been considerable interest in the area of theoretical studies of the electronic conductivity of GICs [27–31]. It is neither intended, nor possible, to cover all these developments in a single review. Hence, the present discussion is mainly confined to the electrochemical aspects of GICs.

Electrochemical methods have been used for the synthesis of GICs for the past several decades [32]. The real interest in this area picked up after the commercial success achieved in lithium/graphite fluoride, primary battery systems in 1970s [33]. In these systems, however, GIC is formed during discharge. The recent search for a practical secondary battery system without a lithium metal anode rekindled interest in GICs. Among the variety of host lattices [20] that are being evaluated, graphite still retains its predominance as a host lattice for cationic and anionic intercalation [21] and thus covers a wide potential range. This factor is responsible for the many recent efforts to develop intercalation batteries with graphite anodes and cathodes. The present review is an attempt to cover these developments in a comprehensive fashion.

Though electrochemical application of GICs is the main area towards which the current review is focused, an attempt is made to introduce the subject matter in different

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Table 1

The short history of graphites intercalation compounds (modified and updated from Table 1 of Ref. [2])

Year	Topics
1841	H ₂ SO ₄ -GIC (Schafhaut 1)
1926	K-GIC (Cadenbach)
1930	Graphite fluorides (Ruff, Keim)
1932	FeCl ₃ -GIC (Thiele)
1964	K-H-GIC (Saeher)
1969	Daumas-Herold model (Daumas)
1972	High conductivity of GICs (Ubbelohde)
1974	Li/(CF) _n primary battery (Fukuda)
1976	High conductivity of MF ₃ -GICs (Vogel)
1981	Ni(OH) ₂ -GIC secondary cell (Flandrois)
	Ionic fluorine-GICs (Nakajima)
1987	Metal chloride-GICs by molten salts (Inagaki)
1991	Alkali metals-GIC (Maeda)
1992	Rocking-chair type intercalation (Guyomard)
1994	Dual intercalation-molten salt (Carlin)
1995	Dual intercalation-non-aqueous medium (Santhanam, Noel)

stages. A broad outline of the structure and the terminologies involved in graphite intercalation chemistry are introduced in Section 2. General methods of preparation (Section 3) and characterization (Section 4) of GICs are then presented with suitable examples selected as far as possible from electrochemical literature. The intercalation/deintercalation behaviour of single electrodes is reviewed in Section 5. This is followed in Section 6 by a discussion of battery systems that are commercially available and those promising systems that are still the subject of research.

2. Outline of the structure of graphite intercalation compounds

McCreery [34] has presented a simple, lucid and illustrative discussion on graphite and other carbon materials employed in electrochemistry. Graphite materials generally contain polyaromatic rings with sp² carbon atoms. These aromatic planar rings are stacked together by π-π interaction of the electronic network. The planar layer formed by the aromatic ring system is generally termed a basal plane. The axis perpendicular to the basal plane is called the C-axis. Electron transport through the C-axis is primarily responsible for the conductivity of graphite. Two size parameters, namely, the length of the graphite material in the basal plane (*L_a*) and the length or thickness of the C-axis (*L_c*), are commonly used to distinguish different types of graphite materials. Four typical carbon materials that contain sp² carbon stackings and that are widely used in electrochemistry are presented in Fig. 1. Highly-oriented pyrolytic graphite (HOPG) generally possesses large *L_a* as well as large *L_c* values (Fig. 1a). Glassy carbon electrodes (GCE) contain relatively thin strips (small *L_a*) of graphite layers. The method of preparation of GCE from polymeric material also ensures low porosity and high compactness

for this material (Fig. 1b). Carbon fibres also consist of highly-oriented graphite layers, but these fibres are very thin (in the μm range) as their name implies (Fig. 1c). Commercially available graphite electrodes possess smaller *L_a* and *L_c* values in general and the particles possess very little orientation (Fig. 1d).

The large π-electronic network in graphite can either be oxidized or reduced quite easily. When an electronegative species accepts an electron and forms an ionic bond with this π-electronic network (represented by C_x below) an acceptor-type GIC is produced, i.e.,



In contrast, a metal atom can donate an electron to the network and form a donor-type GIC, i.e.,



One can imagine a ternary graphite intercalation system that contains more than one type of donor, acceptor, or even mixed donor-acceptor ternary systems. On most occasions in electrochemical intercalation processes, the solvent or acid molecules also get co-intercalated with the acceptor or donor species. In principle, these systems are also ternary systems.

The term 'stages' in intercalation nomenclature [35–37] essentially refers to the number of graphite layers that lie between alternate intercalant layers. Hence, stage 1 is the GIC system with the highest level of intercalant concentration (Fig. 2a). The stepwise formation of GICs of increasingly higher concentration can, for example, be detected

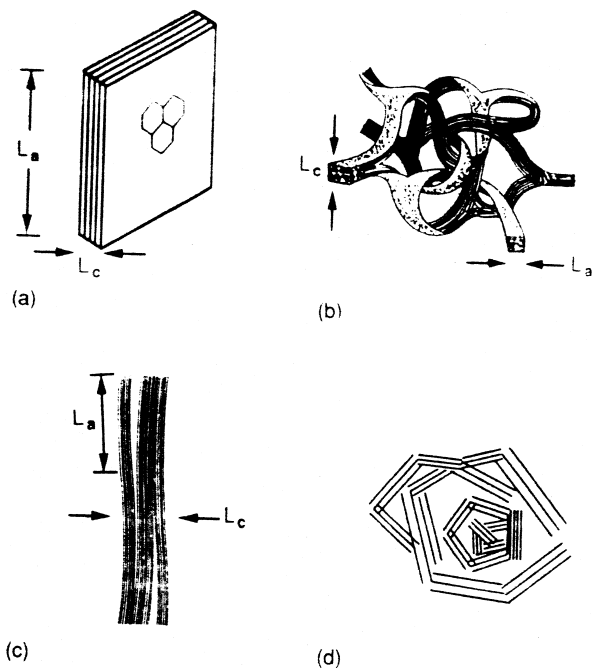


Fig. 1. Four types of sp² carbon (drawings not to scale): (a) HOPG; (b) glassy carbon; (c) carbon fibre (edge view); (d) carbon black [34].

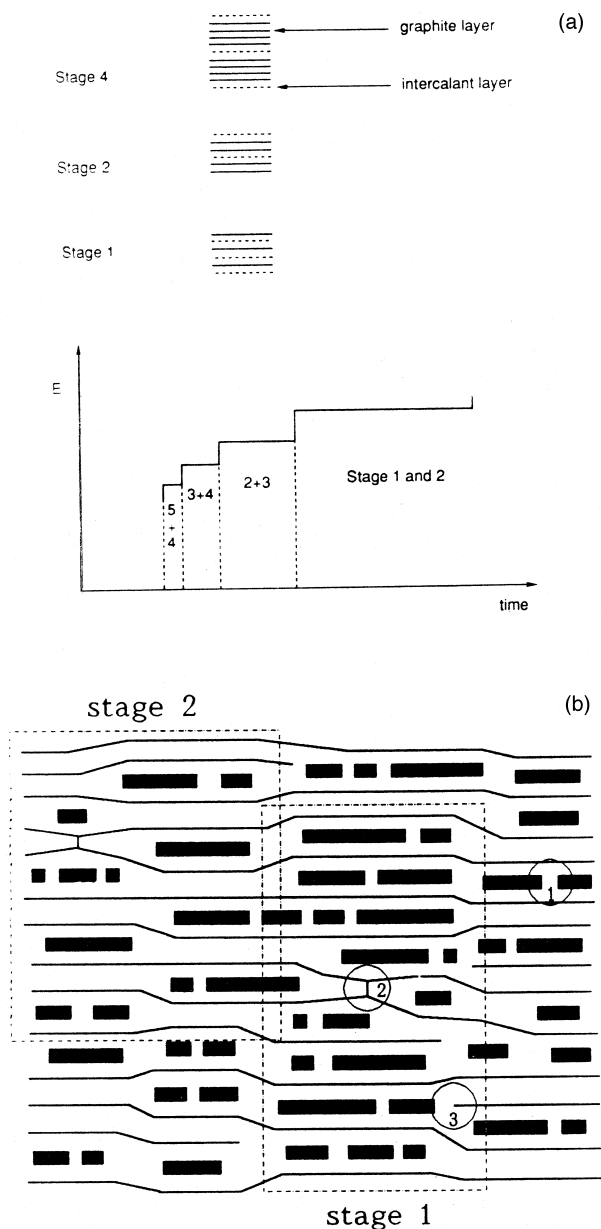


Fig. 2. (a) Potential vs. time plot during galvanostatic intercalation; numbers denote stages of intercalation [34]. (b) Defective intercalate with areas of statistical stacking order and areas of stage 1 or stage 2 order. Boundaries of guest islands are seen at location '1', an interlayer defect in graphite is shown at '2', a terminating graphene layer causing a domain boundary in the GIC appears at '3' [21].

by the stepwise increase in potential during the preparation of GICs under galvanostatic conditions.

In defining the stages in GIC systems, it is assumed that the graphite material is defect-free and the guest species intercalate as a continuous phase in the graphite lattice. Both these conditions are rarely met in reality. The graphite layers themselves may contain a number of defects and grain boundaries, even in the highly-oriented pyrolytic graphite material. The guest species may intercalate into different layers and transform graphite layers into different

exfoliated stages. The size of each island of the guest species may also be different. A typical non-ideal system containing stages 1 and 2 is shown in Fig. 2b. This model is generally termed the Daumas–Herold model [38].

Ideally, it is desirable to have GICs, which could reversibly intercalate and de-intercalate without any damage to the graphite lattice, at least for electrochemical applications. In real systems, however, this is hardly possible. During oxidative intercalation of graphite in H_2SO_4 media, for example, oxide formation in the bulk of the GIC system can cause irreversible damage to the graphite lattice (Fig. 3a). The disintegration of the graphite lattice during electrochemical intercalation/de-intercalation depends on a number of parameters such as the potential limit, solvent, the size and concentration of the intercalant species, etc. Both L_a and L_c parameters can thus undergo significant changes during the intercalation/de-intercalation processes. The form of the disintegrated lattice may be significantly different, even in a starting graphite host material with ideal orientation (Fig. 3b).

With polycrystalline systems, such as commercially available graphite electrode materials, the graphite particles on the electrode surface, can be assumed to have quite different orientations. In contrast to the basal planes that expose the relatively stable π -electronic system, the edge

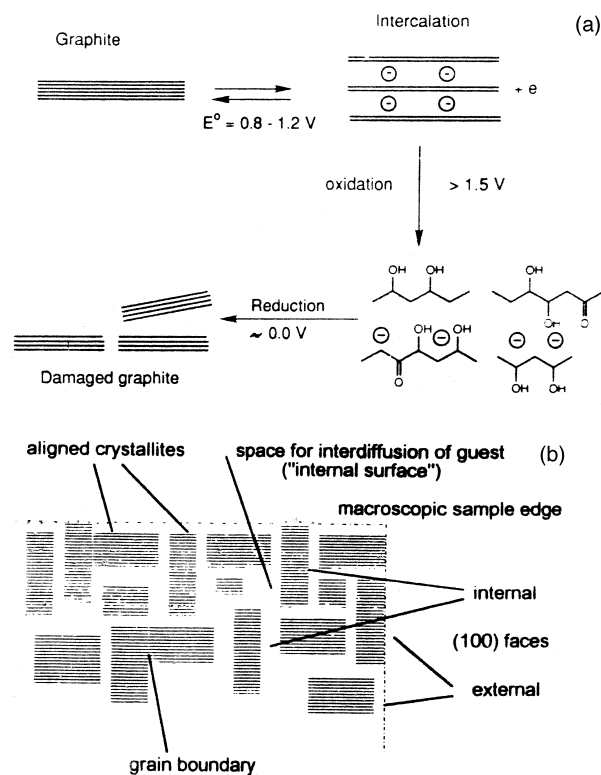


Fig. 3. (a) Schematic representation of structural changes that occur during oxidation of graphite in strong H_2SO_4 . Small circles denote HSO_4^- ions [34]. (b) Composition of a macroscopic graphite sample from crystallites allowing inter-diffusion of guest species (also from the ideally non-reactive basal planes) after mechanical disintegration has opened the crystal [21].

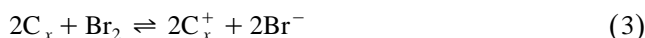
planes (which are more reactive) can undergo facile oxidation and lead to a variety of oxidized surface functional groups. This can also influence significantly the reversibility of the intercalation/de-intercalation processes.

While discussing the chemistry of GICs, it is important to remember that a wide range of non-ideal situations can arise during individual experimental work. The discrepancy between the results reported by different laboratories may also be understood mostly on these grounds.

3. Methods of preparation

3.1. Chemical methods

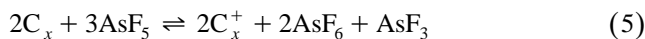
Treatment of graphite powder with the intercalant vapour at high temperature is an efficient method for preparing acceptor-type GICs. This method has recently been extended for intercalating bromide into graphite fibres [38,39], through exposure to Br₂ vapour which also acts as an oxidizing agent, i.e.,



The oxidative intercalation may proceed as a reversible charge-transfer process without chemical transformations, as in the case of OsF₆ [40]:



On the other hand, significant chemical changes can accompany the intercalation, as found with AsF₆ [41]:



Fluorine reacts vigorously with graphite materials. Passage of nitrogen-diluted fluorine gas under controlled conditions through graphite powders generally results in covalent graphite fluorides [42]. Depending on the operating conditions, especially temperature, two types of covalent graphite fluorides are obtained, namely, (C₂F)_x and (CF)_x. These materials, which were mainly responsible for the development of the first commercially successful lithium/graphite fluoride battery system, have been thoroughly studied and extensively reviewed by Watanabe et al. [42]. Although graphite fluoride is not an intercalation compound, in a battery system the discharged product is essentially an intercalation compound (Section 5.3).

In the presence of anhydrous HF or other metal fluorides, graphite reacts with fluorine at room temperature to form a fluoride-intercalated GIC [43,44]. The formation of GICs of this type is facilitated by exfoliating the graphite lattice prior to intercalation through, for example, graphite oxide [45,46].

Molten electrolyte media [47,48] are quite convenient for intercalating metals and metal salts of low volatility, such as CuCl₂, NiCl₂ and FeCl₃, and also for simultaneous intercalation of more than one halide species [49] into the graphite lattice. Complete experimental details for this

method are available [47–50]. It is also possible to investigate the structural transformations of GICs that are formed by differential thermal analysis [51].

Strong acids with sufficient oxidizing power, e.g., H₂SO₄ and HNO₃, can be used directly for intercalating the graphite. In these cases, the acids serve as intercalating oxidants as well as solvents. Since excess acid is always present during intercalation, the acid molecules are also trapped with intercalant anions to form compounds such as C_x⁺ HSO₄⁻ (H₂SO₄)_y. This is one of the simplest methods that has found industrial application in supercapacitors.

Some interesting intercalation studies have been carried out in aprotic solvents such as nitromethane and tetramethylene sulfone [52,53] and strong protic solvents such as fluorosulfuric acid [54]. It is also possible to intercalate inorganic salts such as NiCl₂ using organic solvent [55]. Comparative evaluation of graphite intercalation using liquid HF and vapour phase HF has also been reported [56].

3.2. Electrochemical methods

Under appropriate experimental conditions, graphite can be electrochemically oxidized or reduced to give C_x⁺ and C_x⁻ lattices which can hold anionic or cationic species, respectively. In an appropriate solvent supporting electrolyte system, a wide potential window of +2.5 to -2.5 V is accessible for intercalation into this unique host lattice. Both acceptor and donor type GICs have been synthesized for many decades by this method [3–14] [15–18].

Beck et al. [57–59] introduced a polypropylene-based graphite which showed good stability during intercalation/de-intercalation processes. Electrochemical intercalation in a graphite particulate system [60] and carbon fibres [61], as well as evaluation of intercalation levels by potential–time relations [62], have also been reported.

Many other electrochemical approaches and electrochemically intercalated GIC systems have been investigated. These include synthesis of a graphite bi-intercalation compound in a H₂SO₄, H₂SeO₄ mixed system [63], Li ion intercalation in butyrolactone media [64], electrochemical intercalation of fluoride in aqueous [65–69] and anhydrous HF media [70,71], conversion of a NiCl₂-based GIC into a more useful Ni(OH)₂-based GIC by electrochemical polarization in alkaline media [72], electrochemically induced intercalant exchange [73], comparison of the electrochemical behaviour of GICs with polyacetylene [74], and efficient intercalation studies in molten electrolyte media [75–77].

3.3. Photochemical methods

Apart from chemical and electrochemical methods, oxidation or reduction of the graphite host lattice may also be

achieved by the photolysis of the intercalant precursor or solvent molecule. The rate of intercalation can be controlled carefully by choosing appropriate photochemical parameters. Hence, these methods are used to study the structure and detailed dimensional picture of intercalant island layers in the graphite lattice [78–80]. To date, this method appears to be used only for basic investigations and has not been involved in device development.

4. Characterization of graphite intercalation compounds

GICs are reasonably sophisticated, three-dimensional, solid-state materials. In the *C*-axis of the single crystal material, it is possible to visualize different stages of intercalation, different exfoliation pathways, and different sizes of intercalated regions. The host material can contain different solid-state defects. The edges exposed to the open atmosphere may possess different surface activities. Polycrystalline and composite graphite materials may be employed. The guest species itself may be a simple ionic, solvated ionic or complex ionic species. In such a complex situation, GIC characterization becomes a formidable task.

Nevertheless, a wide variety of experimental techniques are currently available to study GICs (Table 2). From the application point of view, simple electrochemical techniques provide capacity data as well as charge/discharge characteristics. More sophisticated techniques, such as cyclic voltammetry and impedance spectroscopy, may pro-

vide the interfacial kinetics and the impedance characteristics of the battery system.

Intercalated stages, surface exfoliation and other irreversible surface transformations may be evaluated using microscopic techniques. Scanning electron microscopy (SEM) has been in use for quite a long time. At present, tunnelling electron microscopy (TEM) and scanning tunnelling microscopy (STM) are used to identify intercalation domains and even line defects. Obviously, SEM can also be used to characterize the host lattice before intercalation.

X-ray diffraction (XRD) is probably the most widely used technique for characterizing the host lattice as well as GICs formed from these host lattices. Many modified versions of XRD techniques are also currently employed to analyze localized regions of GICs and even for in-situ characterization.

Thermogravimetry (TG) and differential thermal analysis (DTA) provide information on the material structure as well as energy transformations involved in the de-intercalation process. Recently, a wide variety of spectroscopic techniques that range from infrared to Mossbauer and X-ray photoelectron spectroscopy have been applied to the investigation of GIC materials.

A comprehensive review of the structural aspects of GICs that covers most of the techniques listed here is available [19]. In electrochemical studies, however, only a few conventional characterization techniques are repeatedly employed. A brief account of these techniques with a few examples follows.

Table 2
Some important techniques for the characterization of graphite intercalation compounds

Method	Inference	Refs.
<i>I. Electrochemical</i>		
1. Galvanostatic experiment	Stages of intercalation	[81]
2. Potentiostatic experiment	Charge	[65]
3. Cyclic voltammetry	Intercalation reversibility; charge	[65]
<i>II. Microscopic</i>		
1. Scanning electron microscopy	Surface transformations of intercalated material	[82]
2. Transmission electron microscopy	Direct image of domain boundaries	[83]
3. Scanning tunnelling microscopy	Line defects	[84]
<i>III. Diffraction</i>		
1. X-ray diffraction		
a. In situ diffraction experiment	Cascades of stages from high to low	[85]
b. Spatially resolved diffraction experiment	Reaction zones of different stages within a single crystal of graphite	[86]
c. Monochromated laue X-ray diffraction experiment	In-plane structural exploration of GIC	[87]
<i>IV. Thermal</i>		
1. Thermogravimetry	Weight loss of intercalated material	[88]
2. Differential thermal analysis	Exothermic and endothermic reactions of intercalated material	[88]
<i>V. Spectroscopic</i>		
1. Raman spectroscopy	Polymerization of guest	[89]
2. Ultraviolet photo emission spectroscopy	Chemical bonding in GIC	[90]
3. Electron spectroscopy for chemical analysis	Shifts of the Fermi edges of GIC relative to the vacuum level	[91]
4. Mossbauer spectroscopy	Presence of different species in the light and dark areas of the sample	[92]

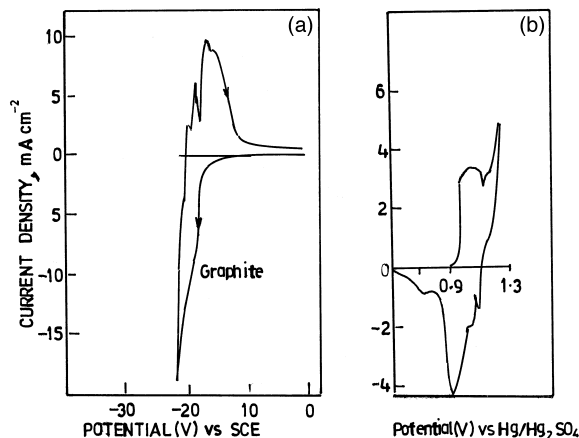


Fig. 4. Cyclic voltammograms of (a) graphite foil in 1.0 M LiClO₄ in DMSO; scan rate = 5 mV s⁻¹; (b) natural graphite flake (contains 20 wt.% polypropylene) in 4.0 M HClO₄; scan rate = 1 mV s⁻¹ [58,94].

4.1. Cyclic voltammetry

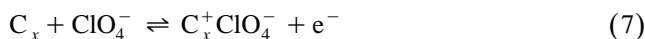
Cyclic voltammetry (CV) is a simple and versatile electroanalytical technique which is now routinely employed to evaluate any faradaic process [93]. This technique is also used for a quick assessment of the formation as well as the stability of GICs.

The typical cyclic voltammetric response (sweep rate = 5 mV s⁻¹) for a graphite electrode in DMSO that contains 1.0 M LiClO₄ and is shown in Fig. 4a [94]. The intercalation reaction is:



In this case, charging occurs at relatively high current density and, probably, simultaneous decomposition of solvent supporting electrolyte also occurs along with the charging process. The cathodic discharge peaks are invariably distinct and are due to the de-intercalation of different stages of intercalation compounds.

A typical cyclic voltammogram of graphite in 4.0 M HClO₄ acid recorded at a sweep rate of 1 mV s⁻¹ is presented in Fig. 4b [58]. During the anodic sweep, the anodic current is found to increase around 1.0 V due to the intercalation of perchlorate anion on the electrochemically oxidized graphite lattice, i.e.,



The corresponding de-intercalation peak occurs at around 0.8 V. The X-axis in the cyclic voltammogram may also be considered as a time axis because potential varies linearly with time. Hence, the areas contained under the anodic and cathodic segments in the cyclic voltammogram correspond to the intercalation charge (Q_{in}) and the de-intercalation (Q_{di}) charge, respectively. The ratio, Q_{di}/Q_{in} , represents the charge recovery, or rather the reversibility of the intercalation/de-intercalation processes in a single cycle.

Cyclic voltammetry can be conveniently used to study the effect of the electrolyte medium, the solvent, different salts containing intercalating anions or cations, and other operating variables on the overall intercalation/de-intercalation efficiency (IDE).

4.2. Potentiostatic and galvanostatic charging curves

The intercalation process is usually carried out at selected potentials that are obtained from preliminary cyclic voltammetric studies. Typical current–time transients obtained at different potentials for graphite electrodes in 4.0 M HClO₄ are presented in Fig. 5a [58]. Integration of the areas under these current–time transient curves provides the respective intercalation charges (Q_{in}). The de-intercalation charge (Q_{di}) can also be obtained by holding the electrode at the corresponding de-intercalation potential. Hence, the charge recovery ratio can be calculated.

Batteries are essentially operated under galvanostatic or constant-current conditions. Consequently, charge/discharge curves under such galvanostatic conditions are also important. A typical potential–time curve for a graphite electrode in H₂SO₄ medium (HSO₄⁻ ion intercalation) is shown in Fig. 5b [81]. The intercalation potentials for each

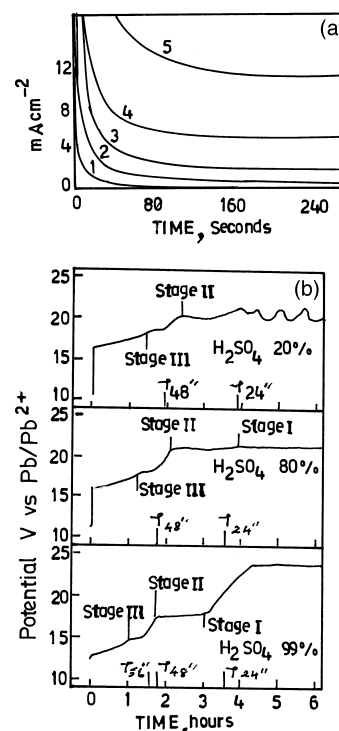


Fig. 5. (a) Current–time curves with natural graphite flake (contains 20 wt.% polypropylene) in 4.0 M HClO₄, freshly scraped, for potentiostatic switch from $E_s = 900$ mV to: (1) $D_s = 1000$ mV ($\Delta E_s = 100$ mV), (2) $E_s = 1100$ mV ($\Delta E_s = 200$ mV), (3) $E_s = 1200$ mV ($\Delta E_s = 300$ mV), (4) $E_s = 1300$ mV ($\Delta E_s = 400$ mV) and (5) $E_s = 1400$ mV ($\Delta E_s = 500$ mV) [58]. (b) Constant current oxidation (~ 25 μ A per mg graphite) of HOPG in H₂SO₄ of different concentration (wt.%). Roman numeral denotes completion of the indicated stage [81].

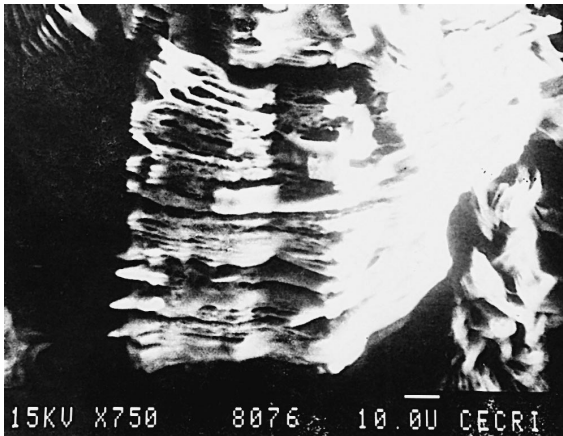


Fig. 6. The electron micrograph showing the exfoliated layer structure of ClO_4^- ion intercalated polypropylene graphite composite sample [82].

stage of the GICs can be clearly seen. Calculation of the intercalation charges ($Q_{\text{in}} = It$) is also very simple with this method.

4.3. Scanning electron microscopy

Imprints of exfoliation processes can be readily identified by SEM. A typical electron micrograph of graphite that has been exfoliated through ClO_4^- intercalation is presented in Fig. 6 [82]. Such exfoliation under mild conditions increases the surface area of the graphite lattice and thus enhances the intercalation/de-intercalation processes to some extent. It should be noted, however, that severe exfoliation can cause irreversible surface transformation. The latter can also be examined with SEM.

4.4. X-ray diffraction

A typical XRD pattern of a HOPG electrode, cathodically polarized in DMSO that contains magnesium chloride, is presented in Fig. 7 [95]. The electrode polarized at -1.6 V contains XRD lines that correspond to graphite in addition to new lines that correspond to the GICs (Fig. 7a). With stronger electrochemical intercalation at -2.2 V, the XRD lines due to graphite completely disappear (Fig. 7b). Such strong XRD signals are difficult to obtain for polycrystalline graphite material. The XRD peak intensity of the GICs may be as low as 1 to 5%. Nevertheless, such XRD spectra are used as fingerprints to identify specific GICs.

4.5. Thermogravimetry and differential thermal analysis

Thermogravimetry measures the change in the weight of any material as a function of linearly increasing temperature. This weight loss indicates decomposition or evaporation of the sample. The temperature range in which no

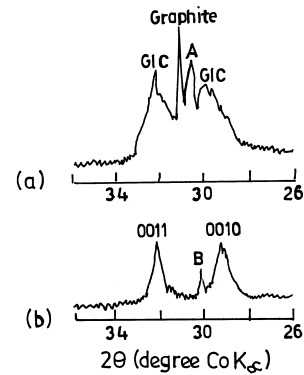


Fig. 7. The X-ray diffraction pattern of highly oriented pyrolytic graphite electrolyzed cathodically at constant potential: (a) -1.6 V for 12 h; (b) -2.2 V for 48 h [95].

weight loss is noticed is the region where the sample in that particular form exhibits thermal stability. The TG curve of a hypothetical sample is shown in Fig. 8a. The physical properties of chemical compounds can be ascertained from these studies.

Differential thermal analysis measures the rate of change of the temperature of a sample as it is heated at a constant

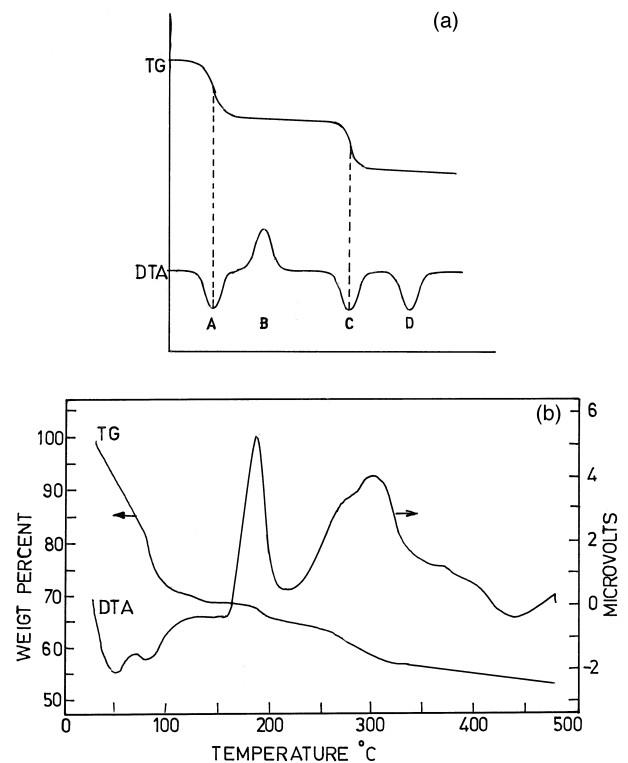


Fig. 8. Thermogravimetry and differential thermal analysis curves. (a) A hypothetical sample. The two steps in the TG curve result from weight losses and correspond to peaks A and C in DTA curves. Peaks B and D are exothermic and endothermic, respectively. (b) polypropylene-graphite composite electrode electrolyzed cathodically at a potential of -2.5 V for 5 h. Speed of rise in temperature = 5°C min^{-1} [96].

rate. In the course of heating, the sample can undergo a phase transition or weight loss. An endothermic reaction absorbs heat and the DTA response is negative. An exothermic reaction releases heat and the peak is positive (Fig. 8a).

The typical TG and DTA curves for a Li^+ -intercalated graphite sample [96] are presented in Fig. 8b. The TG graph shows distinct weight-loss regions over the temperature range 30 to 500°C . DTA shows some endothermic processes below 150°C . These endothermic processes have been attributed to solvent evaporation from the surface of the intercalated sample. Exothermic peaks are observed over the temperature range 150 to 350°C . These exothermic peaks are associated with solvent evaporation from the interior of the graphite sample.

4.6. Electron spectroscopy for chemical analysis (ESCA)

Spectroscopic techniques are less commonly employed in GIC electrochemistry. ESCA, however, has found interesting application, in distinguishing between covalent graphite fluorides ($\text{C}_x - \text{F}$) and ionic fluoride intercalated GIC ($\text{C}_x^+ \text{F}^-$).

ESCA spectra of GICs before and after grinding in an agate motor [97] are presented in Fig. 9. The C_{1s} spectra have a main peak at 284.3 eV. This peak corresponds to carbon that has an ionic bond with fluorine and to that unbound with fluorine. The peaks shifted to around 289 eV are close to the position of the C–F covalent bond peak observed in graphite fluoride. The peak for the F_{1s} electrons, at 688 eV, is also close to that for a C–F covalent bond. On the other hand, the ground samples indicate that the C_{1s} peak at 289 eV is decreased and a new F_{1s} peak clearly appears at 685.8 eV in the vapour grown carbon fluoride (VGCF) compound. The latter is close to the position of a fluoride ion in LiF (684.5 eV). Thus, several surface layers are strongly fluorinated, but the intercalated fluorine possesses a nearly ionic bond with carbon atoms inside the GIC.

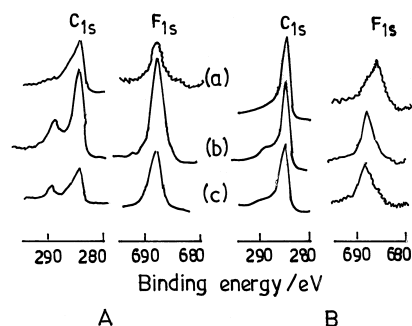


Fig. 9. The ESCA spectra of fluorine-carbon fibre intercalation compound prepared in the presence of CuF_2 : (A) as prepared; (B) after grinding; (a) VGCF-based GIC, $\text{C}_{9.5}\text{F}$, (b) pitch fibre-based GIC, $\text{C}_{8.7}\text{F}$; (c) PAN fibre-based GIC, $\text{C}_{10.1}\text{F}$ [97].

5. Electrochemical studies

Individual intercalation/de-intercalation studies and evaluation of cycling efficiency have been carried out for many anionic and cationic species. No effort is made here to review all these studies comprehensively. Instead, a few examples that have specifically been evaluated for commercial applications alone are considered briefly. Graphite fluorides are essentially covalent compounds. Nevertheless, the discharge product of this material is essentially an intercalation compound. Hence, a brief outline of the electrochemical behaviour of this system is also discussed.

5.1. Anionic intercalation

Sulfuric acid based GICs have been synthesized and characterized since 1938 [32,98]. Compared with pure graphite material, a polypropylene graphite composite containing 20 wt.% polypropylene as a binder is found to exhibit better stability and superior reversible charge/discharge behaviour [58,59,99–101]. Good intercalation performance in H_2SO_4 , HClO_4 , HBF_4 and HF media has also been reported [58,59]. Corrosion behaviour over long duration [99] and acid concentration dependence of intercalation potentials [100,101] have been evaluated. The latter studies, for example, have indicated the possibility of using the H_2SO_4 -graphite electrode as a pH sensor in strong acid media. Finally, staging transitions in H_2SO_4 -graphite [102] and hydrolysis of HClO_4^- and H_4SO_4 -based GICs have been reported [103].

Fluoride intercalation in aqueous HF media [58,59] have been used successfully to assemble a lead/graphite accumulator [104,105]. Fluoride intercalation from anhydrous HF [105,106] and molten fluoride media [106] has also been examined. The effects of different mixed aqueous solvents on the intercalation/de-intercalation efficiency of fluoride ions on graphite electrodes have been examined [66,68]. Aqueous-methanolic mixtures are found to be a better choice for improved intercalation/de-intercalation efficiency and also good stability towards cycling [67]. A thin polypyrrole layer coated on graphite before intercalation further improves the stability of graphite electrodes [65].

Since anion intercalation is quite efficient in strong aqueous acid media, only a few studies have been made of this process in non-aqueous solvents. Perchlorate anion intercalation on graphite electrodes in propylene carbonate media was reported as early as 1978 [107]. The use of this system as a positive electrode in lithium secondary cells has also been explored [108]. Anodic intercalation and cathodic de-intercalation of perchlorate anions were shown to cause exothermic and endothermic changes, respectively, in differential thermal analysis [109]. The intercalation behaviour of perchlorate and fluoborate anions from

propylene carbonate and acetonitrile solvents on polypropylene graphite electrodes was discussed recently [96].

5.2. Cationic intercalation

In most cases, oxygen evolution is the competitive process for anionic intercalation on graphite electrodes. Since the overvoltage for oxygen evolution from water on graphite itself is fairly high, competitive anionic intercalation is quite efficient from aqueous solutions. For cationic intercalation, however, hydrogen evolution from aqueous solution (especially acidic solutions) is more facile. Thus, it is generally impossible to achieve good intercalation/de-intercalation efficiency for cations in aqueous solutions.

In non-aqueous solutions, however, the intercalation/de-intercalation process is quite efficient. Besenhard and Fritz [110] investigated the electrochemical intercalation of alkali metal cations from a number of non-aqueous solvents [110]. A proposal for a non-aqueous secondary battery was also advanced [111]. Subsequently, tetraalkylammonium cations were found to give intercalation/de-intercalation responses which were similar to those of alkali metal cations [94,112]. Graphite fibres were also found to show good intercalation behaviour [113]. The electronic properties of these cation-intercalated graphite electrodes have been investigated in detail [114].

Maeda and Harada [115] co-workers have studied cationic intercalation on carbon fibre electrodes in DMSO. The thermal behaviour of electrochemically intercalated graphite has also been reported by Maeda [116] and Maeda et al. [117]. A general evaluation of vapour phase as well as electrochemical intercalation of alkali metal cations is available [118]. Intercalation and de-intercalation studies from mixed-solvent systems that contain ethylene carbonate and propylene carbonate have been reported [119]. Careful evaluation of the structure of solvated intercalant is receiving attention in recent times. The potassium ion-tetrahydrofuran (K^+ -THF) intercalant system may be cited as an example [120]. Among DMSO, DMF and PC, the later is found to show better intercalation/de-intercalation efficiency for Li^+ as well as tetrabutylammonium cations [96].

With larger tetraalkyl ammonium cations, irreversible surface damage becomes predominant [121]. Tetra-*n*-octyl ammonium cation is a typical example for such behaviour. It appears that the relatively smaller tetraalkyl ammonium cations enter into the graphite lattice without solvation spheres. Thus, lattice expansion during intercalation remains in the reversible transformation range.

Apart from the monovalent cations discussed so far, electrochemical intercalation/de-intercalation behaviour of some divalent cations such as magnesium (Mg^{2+}) and manganese (Mn^{2+}) have also been reported in non-aqueous solvents [88,95].

5.2.1. Lithium intercalation

Due to the current interest in rechargeable lithium-ion batteries, Li^+ intercalation has become an important area of active research. A variety of host materials that range from Li-Al anodes to $LiNiVO_4$ with vastly different host lattice, Li^+ binding energy are currently under investigation [122] (Fig. 10). Graphite and other carbon materials are among the host lattices with very weak binding energy. Thus, next to Li-Al alloy anodes, Li-GICs have attracted considerable attention.

A wide variety of carbonaceous materials are being evaluated for rechargeable lithium-ion batteries. These include pyrolytic carbon [123] and carbon fibre [124]. The effect of basal and edge planes of highly-oriented pyrolytic graphite has been studied [84]. Different types of graphite materials and their modifications on intercalation efficiency and cycle life have been evaluated [125–127]. Nanodispersed silicon containing carbon materials are found to exhibit increased capacity [128]. The effect of the temperature used in the heat treatment of pitch-based carbon fibres has been evaluated [129]. Polymeric binders in the graphite material, e.g., polypropylene [130] and polyvinylene difluoride (PVDF) [131], are also found to improve the stability of the intercalated system. The thermal stabilities of Li-intercalated carbon anodes and lithium metal anodes have also been compared due to the explosive nature of lithium-alloy anodes [132]. Li^+ -intercalated carbon anodes are finding increasing utility, at least in the case of high-capacity, lithium-ion battery systems.

A variety of solvents has been evaluated for lithium intercalation. Ethylene carbonate, propylene carbonate diethyl-carbonate [133], chloro ethylene carbonate [134] and SO_2 dissolved solvent systems [135] are some of the systems that have attracted current interest. Additives like crown ethers [136] and tetraalkyl ammonium chloride [137], for example, suppress considerably the decomposition of the solvent.

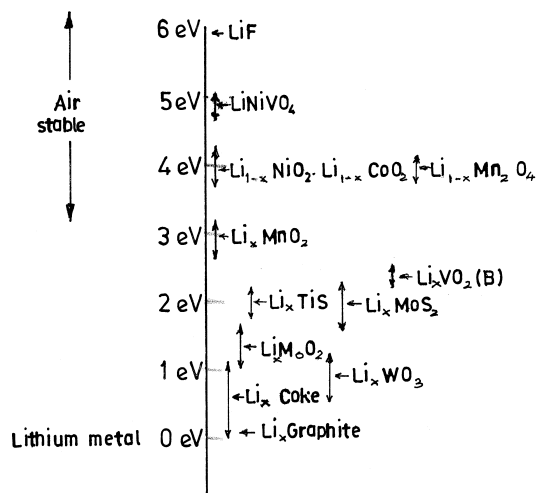


Fig. 10. The binding energy of Li^+ intercalated within a variety of materials. Measurements are relative of that of Li metal [122].

In a recent XRD investigation, a distinctly low inter-layer distance (d) of 3.7 Å in the Li-intercalated GIC was attributed to a solvent-free, binary graphite lithium-intercalation compound [138]. A further careful evaluation of the different stages of lithium intercalation shows that for the stage I compound, the characteristic 'd' value in XRD measurements is 3.7 Å [139]. Whether this stage I intercalation is indeed a solvent-free intercalation remains an open question. Quite advanced in-situ measurements such as in-situ Raman spectroscopy are presently being used in this area [140].

Lithium intercalation studies have also been extended beyond non-aqueous solvents. Good lithium-ion intercalation/de-intercalation is noticed in a polyacrylonitrile (PAN) polymer and ethylene carbonate (EC) mixed electrolyte system [141]. Yazami and Touzain [142] and Yazami et al. [143] have employed a polyethylene oxide (PEO) solid polymer electrolyte for lithium-ion intercalation.

Another interesting medium is the room-temperature chloraluminat melt. Efficient intercalation/de-intercalation of a lithium-ion graphite electrode has been observed in this molten electrolyte media [144].

5.3. Graphite fluorides

Graphite fluorides (see Section 3.1), which are essentially insulating in nature, can undergo facile electrical discharge in the presence of Li^+ ions in aprotic solvent:



This reaction forms the basis for extremely light and efficient lithium graphite fluoride batteries. Such commercial interest has served as a motivation for a thorough investigation of this discharge reaction [42,145–148]. The thermodynamic and kinetic aspects of the reaction, including the solvent effect and Li–F interaction, have also been evaluated [42,145–148].

Recently, there has been considerable interest in converting graphite fibres into graphite fluorides and evaluating the modifications of the physicochemical properties of these fibres [149,150]. There is an interesting report on the thermodynamic properties of fluorine monolayers on graphite [151]. Fluorinating reagents like IF_7 may also be used in place of diluted fluorine gas for graphite fluoride

synthesis [152]. In addition, graphite oxyfluorides have been synthesised and evaluated [153]. Despite these modifications and evaluation of the discharge characteristics, no significant further developments in the original Li–graphite fluoride battery system have been achieved.

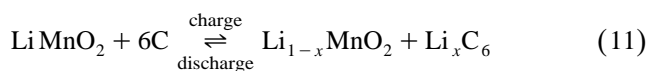
6. Battery systems

Graphite is used as a host lattice in a few successful commercial battery systems. Other systems with promising features are currently under investigation. Typical examples of different types of battery system in which at least one electrode is graphite are summarized in Table 3.

The earliest candidate to use graphite material was the lithium/graphite fluoride primary battery system. In this case, graphite intercalation compound is formed only during discharge, as mentioned earlier, i.e.,



Lithium-ion batteries, commonly referred to as 'rocking-chair' batteries, are attracting great interest. In this system, a metal oxide cathode such as MnO_2 is coupled with Li–Al alloy or graphite anode materials as the host lattice for lithium. Lithium-alloy anodes have the potential to explode due to the presence of lithium metal itself. Hence, at least in higher capacity lithium-ion batteries, graphite has become the host lattice of choice. The charge/discharge reactions (assuming MnO_2 as the cathode material) are as follows.



A very interesting aspect of the rocking-chair battery is the movement of the same Li-ions in opposite directions during discharge (from graphite through electrolyte to MnO_2) and charge (from MnO_2 through electrolyte to graphite) reactions. Hence, no change in the concentration of the electrolyte medium is involved throughout the charge/discharge cycles.

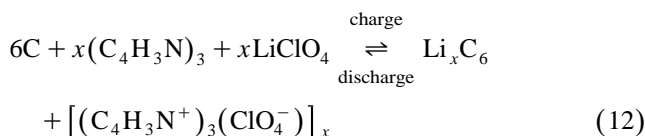
Table 3

Some important intercalation-based battery systems

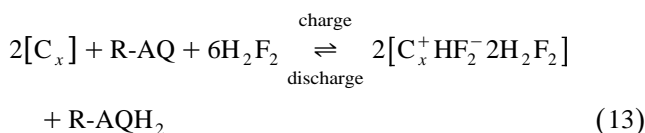
No.	Battery system	Cathode	Anode	Electrolyte	Cell voltage (V)	Refs.
1	Lithium–graphite fluoride	$(\text{CF})_n$	Li	LiClO_4 or LiBF_4/PC	3.2–3.3	[42]
2	Lithium-ion (Rocking-chair)	LiMo_2 (M = Mn, Co, Ni)	Graphite	LiASF_6/PC or EC or MF	3.7	[154]
3	Dual-intercalation (one graphite host)	Conducting polymer	Graphite	LiClO_4/EC –DMC	2.5–3.5	[155]
		Graphite	Anthraquinone	HF	1.7–1.9	[156]
4	Dual intercalation (both graphite host)	Graphite	Graphite	Molten salt	≈ 3.5	[157]
		Graphite	Graphite	TBAP/PC	≈ 3.4	[82]

PC, propylene carbonate; MF, methyl formate; TBAP, tetrabutylammonium perchlorate; EC, ethylene carbonate; DMC, dimethyl carbonate.

Some interesting battery systems involving both cationic and anionic intercalation at the anode and cathode materials, respectively, are being investigated. In such systems, graphite can either serve as an anode or a cathode material. The conducting polymer/graphite system is a typical example where graphite serves as an anode, i.e.,



The graphite/anthraquinone (AQ) based battery system employs graphite as the cathode. Quite interestingly, this system can function efficiently even in aqueous media, viz.,



In these dual-intercalation processes, ion transfer from electrolyte to the two electrodes occurs during charging. This will have significant effect on the overall electrolytic conductivity. As a consequence, these systems require fairly concentrated and highly conducting electrolyte media.

Dual-intercalation systems where graphite can serve as a host cathode and a host-anode have been investigated in recent years. Both molten salt and non-aqueous systems can serve as the electrolyte medium. Fairly large cationic species are found to show good intercalation/de-intercalation efficiency in these systems. More work in this area would be worthwhile.

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