

Electrochemical study of the passivating layer on lithium intercalated carbon electrodes in nonaqueous solvents

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Abstract

Carbonaceous materials are now actively investigated as alternative anodes in lithium rechargeable cells. However, practical problems arise from the electrolyte reactivity at low potential, such as low cycling efficiency during the first charge and high self-discharge rate. The passivation of the carbon is mainly responsible for this initial lack of reversibility, and it was mainly followed by electrochemical methods on carbon tissues that constitute all carbon electrodes of sufficient mechanical stability. The amount of charge necessary to passivate the electrode could be minimized with appropriate choice of electrolyte. Solubilization of the passivating layer in the electrolyte appeared to be the main mechanism of self-discharge and some additives were found efficient for charge retention.

Introduction

In spite of their high energy densities, a large development of rechargeable lithium batteries impinges on the problem of dendritic growth of deposited Li, leading to short cycling life and serious safety problems. A smart solution to overcome these problems consists in using Li intercalation anodes at low potential [1] to constitute the so-called 'rocking chair battery', and some carbonaceous materials have been reported to be extremely suitable in this purpose [2-4]. Another interesting feature of these systems is the possibility of designing anode limited device, as this configuration allows both assembly of the battery in the discharged state with unreactive materials (carbon and lithiated cathode) and harmless overdischarge of the battery down to 0 V. However, the limited diffusivity of Li ions in the host structure, although high for a solid-state reaction (10^{-8} cm²/s in graphite [5]), implies the use of high exchange surface area electrodes and the problem of electrolyte reactivity at low potential is thus enhanced. The low coulombic efficiency observed for the first electrochemical intercalation of Li ion in carbons has been attributed to the reduction of the electrolyte on the electrode surface until deposition of an electronically insulating layer [4], as it is the case on metallic Li. The protective film deposition and its characteristics have dramatic influences on the viability of the battery. The passivating process proceeds through an electrochemical reaction that consumes irreversibly electrolyte and electrons. The latter are taken from the initial capacity of the cathode in battery configuration, and this capacity loss is of primary importance for the energy density of the cell. Moreover, the electronic conductivity and the stability of the passivating layer are the determining parameters for the self-discharge of the electrode. The ideal deposit

must thus be dense and electronically insulating to hinder further electrolyte reduction, must present good conductivity for Li ion and sufficient stability in the operating conditions. The composition of the electrolyte, that yields this protective layer, may have a major influence on its characteristics.

As they constitute all carbon electrodes of sufficient mechanical stability and show reproducible behaviour, carbon tissues were found to be very suitable for the study of the influence of different parameters on the passivating process.

Experimental

Graphitized carbon tissue (Carbone Lorraine) from polyacrylonitrile (PAN) were mainly used as carbon electrodes, petroleum coke (Conoco Inc.) plastified electrodes (5 wt.% polyvinylidene difluoride (PVDF)) were also investigated for comparison. Carbon electrodes were galvanostatically cycled in a three-electrode device with flooded electrolyte and Li reference electrode or in button cells with Li opposite electrode and polymeric separator, more representative of battery configuration. The reduction step was stopped at 0 V to ensure the absence of metallic Li deposition. For button cell configuration, the final charged state thus also depends on the polarization of the Li electrode in the studied electrolyte.

Impedance spectroscopy measurements (Solartron 1250 frequency response analyser and 1286 electrochemical interface) were performed in the potentiostatic mode (30 mV amplitude) around rest potential. This method gave access to an estimation of the electrochemically-active surface area of the initial carbon electrode through double-layer capacitance and to the charge-transfer characteristics at lithiated carbon electrodes. Classical solvents and blends used in metallic Li batteries were investigated as electrolytes: propylene carbonate (PC, Aldrich), ethylene carbonate (EC, Fluka), 1,2-dimethoxyethane (DME, Aldrich), tetrahydrofuran (THF, Fluka), γ -butyrolactone (BL, Johnson Matthey) and dimethylsulfitte (DMSI, Johnson Matthey), LiAsF_6 (Lithco), LiCF_3SO_3 (Fluka) and LiClO_4 (Fluka) were dissolved as conducting salts. Solvents of high purity grade were used without further purification and Li salts were dehydrated under vacuum at 100 °C.

Results and discussion

Impedance measurements on initial carbon electrodes

The wettability and electrochemically-active surface area of the 'fresh' carbon electrode in the electrolytes were roughly estimated by impedance spectroscopy measurements. For such electrodes, the behaviour during impedance measurements can be reasonably approximated by double layer charging and progressive penetration of the alternative current in the porous structure [6]. At high and medium frequency, the contribution of the Li electrode is visible, but at low frequency, the impedance variation is only due to the carbon electrode side. This point has been checked in three-electrode cells. For frequency values below 1 Hz, the observed response approaches a purely capacitive one (Fig. 1), that allows to estimate the electrochemically-active surface area. Calculation yields comparable double-layer capacitance values for carbon tissue whatever the electrolyte and the cell configuration, in the 40–100 mF/g_{carbon} range. Conoco petroleum coke that was reported to yield high reversible capacity (190 mA h/g) for Li intercalation [4] presents higher double-layer capacitance values (Fig. 2) around 650 mF/g_{carbon}.

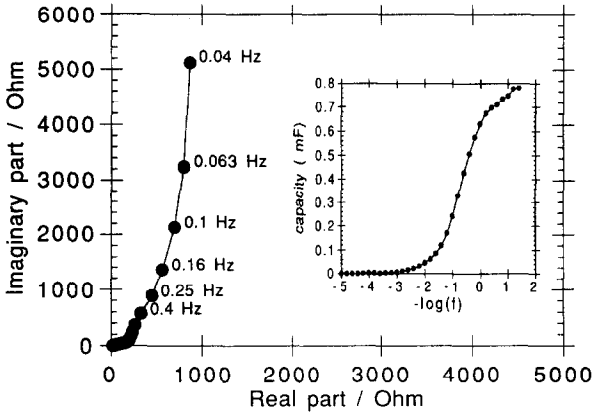


Fig. 1. Impedance spectra of Li-carbon button cells with fresh carbon from 100 000 Hz with five points/decade. Carbon tissue electrode: the behaviour at low frequency approaches a purely capacitive one. Insert: the capacitance calculated from the imaginary part of the impedance nearly reaches an asymptot as a function of the opposite of the logarithm of the frequency.

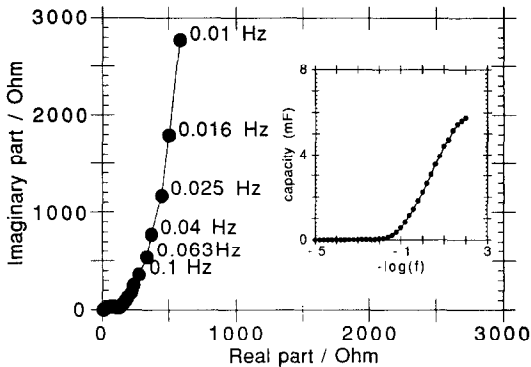


Fig. 2. Impedance spectra of Li-carbon button cells with fresh carbon from 100 000 Hz with five points/decade. Conoco coke 5 wt.% PVDF electrode: the behaviour at low frequency approaches a purely capacitive one. Insert: the capacitance calculated from the imaginary part of the impedance nearly reaches an asymptot as a function of the opposite of the logarithm of the frequency.

Formation of the passivating layer

After reduction of the carbon electrode down to 0 V, capacity was recovered during the oxydation step corresponding to intercalated Li dissolution. Carbon tissues thus actually work as Li intercalation electrodes at low potential but limited capacity is reached. Complete intercalation by long-lasting imposition of 0 V potential only yields LiC_{10} composition, far from LiC_6 theoretical capacity (372 mA h/g). However, the carbon tissue electrodes present other advantages for the study of the passivating process, as the uselessness of any binder and the excellent reproductibility of the electrodes. Moreover, by contrast with graphite that has been reported to exfoliate upon electrochemical intercalation of Li in PC [4], the experimented carbon fibres do not seem to undergo exfoliation. As featured by cyclic voltammetry experiments at

slow scan rate (Fig. 3), exfoliation can be detected on graphite as the current of the first scan is lower than that of the reverse scan. This behaviour is characteristic of an increase in the active surface area of the electrode. This phenomenon is not apparent in the case of graphitized carbon tissue, showing better stability of this carbon electrode. Exfoliation of graphite has been attributed to cointercalation of solvents of good solvating properties for Li ion [4] and may arise either from mechanical strains or subsequent reduction of the solvent with gaseous release in the interlayer space (PC yields propene). It was then stated that solvent cointercalation did not occur at a great extent on the carbon tissue.

During the first cycle, the reactivity of all electrolytes is visible as an irreversible plateau of potential in the reduction step (Fig. 4). When present in solution, AsF_6^- anion also reduces and participates in the passivating process [7], resulting in an additional plateau at higher potential. As the electrode passivation proceeds, the subsequent cycles show good reversibility (Fig. 5) and the deposited layer thus presents sufficient elasticity to withstand the volume variation of the carbon material.

Amount of irreversible capacity during the first cycle

We followed the amount of irreversible capacity during the first cycle, defined as the difference between reduction capacity and oxidation capacity, in different electrolytes (Table 1). This quantity can either arise from electrolyte reduction, surface groups on carbon, Li ion tightly bonded in the structure or carbon material degradation. Its variation with the electrolytes allows to study their relative influence.

However, reliable comparison with the same material implies to reach a similar amount of intercalated Li, as the irreversible capacity was found to depend also on the reversible capacity. In other terms, passivation and Li intercalation are not separate processes. This behaviour is featured in Fig. 6 where the end of charge potential is

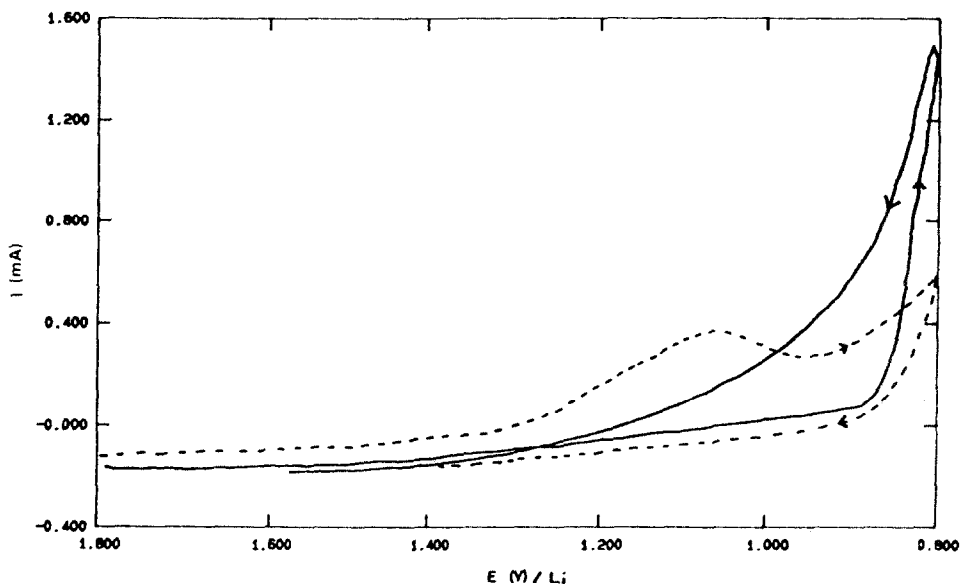


Fig. 3. Cyclic voltammetry at low scan rate (0.1 mV/s) to detect exfoliation of the carbon electrode: (—) natural graphite, and (---) carbon tissue electrode.

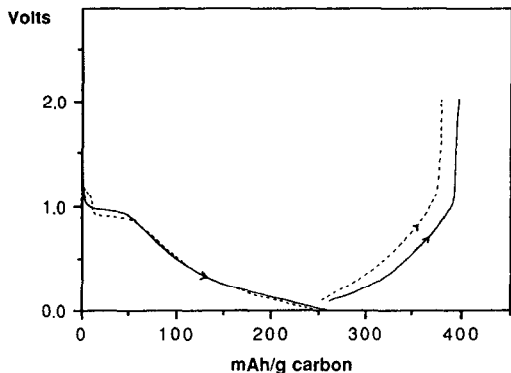


Fig. 4. Electrolyte reduction during the first galvanostatic cycle of Li-carbon tissue button cell at 0.315 mA current (0.5 mA/cm^2): (—) 1 M LiClO_4 in THF - 21 mg carbon, and (---) 1.5 M LiAsF_6 in PC/EC/2DME - 21.2 mg carbon.

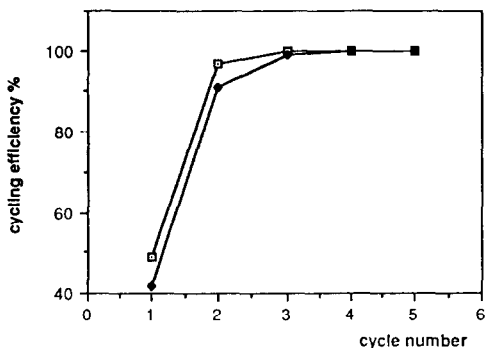


Fig. 5. Coulombic efficiency of Li-carbon tissue button cell at 0.315 mA current (0.5 mA/cm^2): (◆) 1 M LiAsF_6 in PC/EC/2DME, and (◻) 1.5 M LiAsF_6 in PC/EC/2DME.

gradually lowered after reaching 100% cycling efficiency, i.e., after the passivating layer formed is fully protective. Further Li intercalation leads to additional irreversible capacity. This phenomenon is also apparent for Conoco carbon, although less clear (Fig. 7). It is suggested that the additional swelling of the structure induces cracks in the layer, worsened by the release of gaseous products from electrolyte reduction. No clear relation was found with the increase of the interlayer-space parameter taken from ref. 8.

Taking this phenomenon into account, data from Table 1 concerning the characteristics of the first cycle of Li/carbon button cells in different electrolytes can be analysed. The differences in reversible capacity with end of charge at 0 V potential arise from the variation of the polarization of both electrodes with the electrolyte nature. As the passivation can be regarded as a precipitation phenomenon, highly-concentrated solutions seem to favour deposition and stability of the film. CO_2 additive, that improves Li cycling efficiency [9], also presents in the case of the carbon electrode a favourable effect. In spite of their apparently higher active surface area, Conoco petroleum coke electrodes show higher cycling efficiency. It could be attributed either

TABLE 1

Capacities of reduction and oxydation steps for the first galvanostatic cycle of Li-carbon tissue button cell in different electrolytes, 0.315 mA current (0.5 mA/cm²)

Electrolyte	Solvent	Capacity Cr reduction step (mA h/g _{carbon})	Capacity Co oxydation step (mA h/g _{carbon})
1.5 M LiAsF ₆	PC/EC/2DME	253	125
1.0 M LiAsF ₆	PC/CE/2DME	264	110
1.0 M LiAsF ₆	PC/CE/2DME + CO ₂	217	147
1.0 M LiCF ₃ SO ₃	PC/EC/2DME	257	126
1.0 M LiClO ₄	THF	261	135
1.0 M LiAsF ₆	THF	409	141
1.0 M LiAsF ₆	DMSI	402	140
1.0 M LiAsF ₆	BL	391	60
1.0 M LiCF ₃ SO ₃	Conoco 5% PVDF (9 mg) PC/EC/2DME	333	182

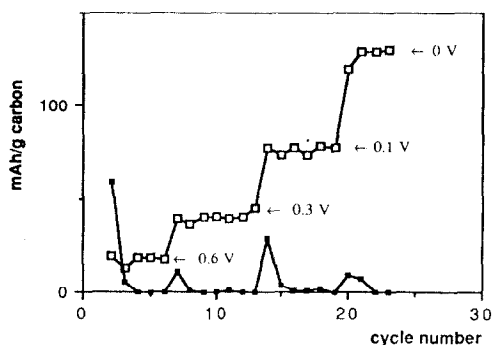


Fig. 6. Progressive Li intercalation by galvanostatic cycling Li-carbon tissue button cell at 0.315 mA (23 mg carbon) in 1 M LiAsF₆ in PC/EC/2DME. End of charge potential: 0.6 V, 0.3 V, 0.1 V and 0 V; (□) reversible capacity and (■) irreversible capacity.

to better adhesion of the layer on the carbon surface or to the faster local saturation and precipitation in the pore structure of the electrode.

Stability of the passivating layer

The passivating layer withstands cycling up to highly oxidizing potentials as the cycling efficiency remains 100% (Fig. 8), confirming that a complete battery can be discharged to 0 V with suitable metallic constituents of the anode. However, if the potential is allowed to rise, oxidation of the electrolyte eventually proceeds and the layer is destroyed (Fig. 8).

Porosity or electronic conductivity of the passivating layer on metallic Li have been often invoked to explain its evolution with time [10]. Because of their high surface area, solubilization of the protecting film in the electrolyte appears to be an important mechanism of self-discharge of carbon tissue electrodes, as confirmed by several observations. After several cycles allowing formation of the passivating layer, the carbon tissue electrode was removed and washed in PC, and assembled in a new

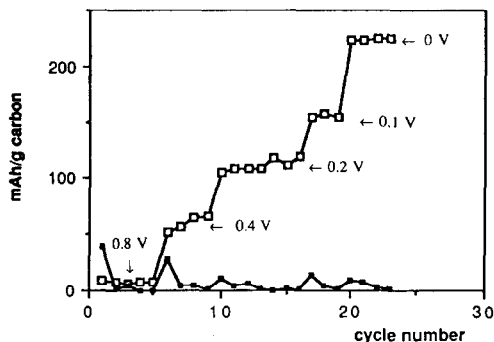


Fig. 7. Progressive Li intercalation by galvanostatic cycling Li-Conoco coke 5 wt.% PVDF cell at 0.315 mA (15 mg carbon) in 1 M LiAsF₆ in PC/EC/2DME. End of charge potential: 0.8 V, 0.4 V, 0.2 V, 0.1 V and 0 V; (□) reversible capacity and (■) irreversible capacity.

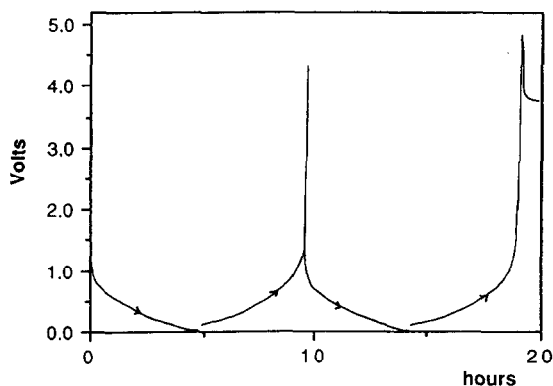


Fig. 8. Stability of the passivating layer at high potential in Li-carbon tissue button cell cycles at 0.315 mA current (20 mg carbon) in 1 M LiCF₃SO₃ in PC/EC/2DME.

button cell. The electrochemical behaviour is then similar to that of fresh carbon tissue, confirming the dissolution of the layer and the minor contribution of surface groups or residual compounds to the irreversible capacity. The self-discharge rate is highly dependent on the electrolyte volume and confinement (Fig. 9): when carbon tissue electrode lithiated in Li/carbon button cell is allowed to rest, the self-discharge is apparent as an increase in the equilibrium potential, accordingly with Nernst relation. The volume of electrolyte in the button cell was estimated to be 0.4 cm³ after weighing of individual components. Transferring the carbon electrode in a 2 cm³ new electrolyte cell without separator yields increased self-discharge, due to higher volume and convection in this configuration.

Other evidences are presented in Table 2, the self-discharge of *in situ* lithiated carbon tissue being completed in one month in flooded electrolyte cell. The high Li ion solvating ability of DME seems to accelerate the solubilization process. However, the self-discharge rate significantly lowers with the ageing of the cell (Table 2), that could be attributed to improvement of passivating layer characteristics, but also to electrolyte saturation in soluble species from the layer. More concentrated solutions of conducting salt also improves the film stability perhaps by limiting its local solubility

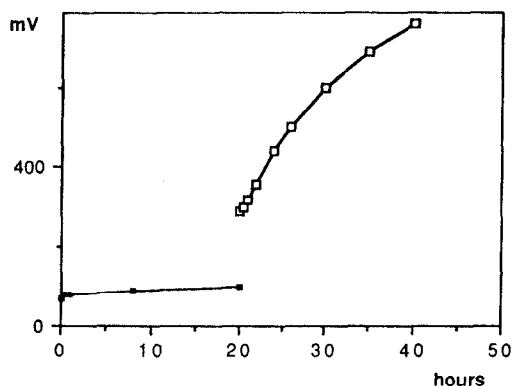


Fig. 9. Evolution of the rest potential during self-discharge of lithiated carbon tissue (22.5 mg) in 1 M LiAsF₆ in PC/EC/2DME; (■) Li-carbon button cell (0.4 cm³ electrolyte), (□) after transfer to a 2 cm³ flooded electrolyte cell.

TABLE 2

One-month self-discharge of LiC₁₇ carbon tissue electrodes at 20 °C in different electrolytes and cell configuration; a: Li-carbon button cell and b: 2 cm³ flooded electrolyte three-electrode cell

Electrolyte	Solvent	First self discharge (%)	Second self discharge (%)	Cell type
0.5 M LiAsF ₆	PC/EC/2DME	11	7.5	a
1.5 M LiAsF ₆	PC/EC/2DME	8	3	a
1.0 M LiAsF ₆	PC/EC/2DME	11	7.5	a
1.0 M LiAsF ₆	PC/EC/2DME + CO ₂	6		a
1.0 M LiAsF ₆	PC/EC	8	5	a
1.0 M LiAsF ₆	PC/EC/2DME	100	58	b
1.0 M LiAsF ₆	PC/EC	33	24	b

('salting out' effect). CO₂ again presents a favourable effect and it appears useful to clarify its action on the modification of the composition of the passivating layer and of its stability.

Other additives reported to improve Li cycling efficiency [9, 11, 12] were experimented (Table 3) either for their tensioactive and adsorption properties (perfluorodecaline) or for their participation in the passivating process.

It thus appears that solubilization of the passivating layer is an important factor of self-discharge, that could be limited by dissolution in the solution of adequate species. However, attention should be paid to the influence of these additives on the cathode behaviour that may invalid this favourable effect in complete cells.

Impedance spectroscopy on lithiated carbon tissues

Lithiated carbon tissue electrodes were characterized by impedance spectroscopy in a three-electrode cell with flooded electrolyte. The impedance measurements were performed in the potentiostatic mode at different stages of galvanostatic cycling of the electrode and they presented good reproductibility during successive cycles. The impedance spectra of a metallic Li electrode were recorded in the same cell configuration,

TABLE 3

One-month self-discharge at room temperature of Li/LiC₁₇ carbon tissue button cells in 1 M LiAsF₆ in PC/EC/2DME with different additives

Additives	self discharge
none	11
CO ₂ (saturated)	6
0.1 M methylthiophene	8.5
0.1 M CH ₃ NO ₂	13
0.1 M propanesultone	10.5
0.1 M perfluorodecaline	9.5

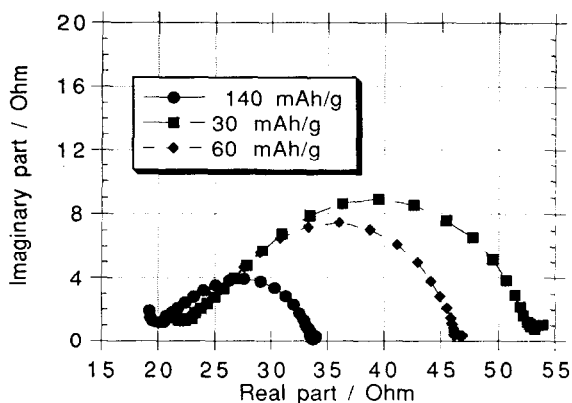


Fig. 10. Nyquist plot of impedance spectra in the 100 000–0.1 Hz range of lithiated carbon tissue in a three-electrode cell with 1 M LiAsF₆ in PC/EC/2DME. Resonance frequencies: 40 Hz (30 mA/g), 66 Hz (60 mA/g), and 164 Hz (140 mA/g).

and yielded a classical depressed semicircle as Nyquist plot, growing with storage time. The generally-accepted interpretation follows the solid-polymer layer model [13], where the observed semicircle is a mixture of three basic loops corresponding to the migration process in the passivating layer (high frequency range), to the charge transfer at the carbon interface (medium frequency range) and to diffusion process within the layer (low frequency range). The increase in total resistance of the loop with storage is interpreted as the increase of the diffusion related loop due to layer growing.

The impedance spectra of carbon tissue also yielded simple depressed semicircles (Fig. 10), but with different characteristics. The total resistance (calculated for the geometric area of the electrode) corresponding to the semicircle decreases with time when the amount of intercalated Li decreases (Table 4). As the exchange-current density at the carbon interface and thus the charge-transfer resistance are dependent on the redox species activities (intercalated Li and Li ion) it is thus stated that the charge-transfer loop is the main contributor to the observed semicircle in these conditions.

In a second set of experiments, the electrode was then allowed to rest after maximum intercalation and impedance spectra were taken at different stages of self-discharge, that presents a high rate in this configuration. The total resistance values calculated during storage (Table 4) are similar to the former ones for the same

TABLE 4

Total resistance of the semicircle (per geometric surface area) in impedance spectra of lithiated carbon tissue electrode during galvanostatic cycling at 0.315 mA current, in three-electrode cell with PC/EC/2DME LiAsF₆ electrolyte. The carbon was also allowed to rest after reaching 140 mA h/g capacity and impedance spectra were recorded at different stages of the self-discharge. The impedance spectra of metallic lithium electrode were recorded in the same conditions

Lithiated carbon tissue capacity (mA h/g)	Loop resistance (Ω cm ₂)	Rest period (days)		
		10	18	
5	143			158
30	23		22	
60	17	20		
140	10			
Li	48	710		880

intercalated Li content and the initial values are restored by galvanostatic cycling. It then seems that in these conditions, the layer thickness remains thin and is continuously destroyed (by dissolution or mechanical removal) and renewed, as confirmed by the high rate of self-discharge in this configuration. The different reactivity of metallic Li and lithiated carbon may induce changes in the characteristics of the deposited layer (density, bonding to substrate, etc.) that could explain the different behaviours.

Acknowledgements

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