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Behaviour of highly crystalline graphites in lithium-ion cells with propylene carbonate containing electrolytes

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Abstract

Several TIMREX® synthetic and natural graphite negative electrode materials with different particle size distributions were tested with regard to their compatibility with propylene carbonate used as electrolyte component in lithium-ion cells. The first lithium insertion properties of these graphite materials were characterised in electrochemical lithium half-cells containing 1 M $LiPF_6$ in ethylene carbonate/propylene carbonate as electrolyte system. *Post mortem* scanning electron microscopy was applied to study the exfoliation process observed for some of these graphite materials especially with coarser particle sizes. X-ray diffraction, Raman spectroscopy and nitrogen gas adsorption were used to characterise and correlate the material bulk and surface properties of the graphite materials with their electrochemical performance. Differential electrochemical mass spectrometry was applied to study the passivation process of the graphite material surface during the first electrochemical reduction. Non-exfoliating graphite materials indicate the formation of an efficient solid electrolyte interphase, which seems to be kinetically controlled by intrinsic properties of the graphite material bulk and surface.

Keywords: Propylene carbonate electrolyte; Graphite exfoliation; Graphite negative electrode materials; Rechargeable lithium batteries

1. Introduction

Graphitic carbon materials are the current materials of choice for the negative electrode in commercial lithium-ion batteries. Among these graphitic carbons, the highly graphitised materials are particularly attractive due to their high reversible specific charge of up to 372 mAh g^{-1}, good cycling stability as well as a high electronic conductivity. The formation of an efficient passivation film on the graphite particle surface during the first electrochemical reduction is essential for the proper functioning of these electrode materials in the lithium-ion battery. This passivation film, the solid electrolyte interphase (SEI), is the key component for the achievement of good reversibility of the electrochemical insertion process, as well as a high energy density and high rate performance [1,2]. The nature of the electrolyte strongly influences the performance of the graphite negative electrode. In particular, not all electrolyte systems are compatible with graphitic carbon-based electrodes. Ethylene carbonate (EC) is known as a good film-forming solvent component in the battery electrolyte [3–5], while propylene carbonate (PC) containing electrolytes are reported to show a rather poor behaviour, especially with synthetic graphite materials [6,7]. Unfortunately, EC cannot be used as single solvent for room temperature applications due to its high melting point, a low viscosity causing low electrolyte conductivities as well as a poor wettability. It has to be mixed with co-solvents to sufficiently enhance its low-temperature performance. Mixtures of EC with dimethyl carbonate (DMC) or diethyl carbonate (DEC) are usually chosen as electrolyte for lithium-ion cells [2,6]. However, PC-based electrolytes are more favourable with respect to their superior low temperature behaviour [4,6,8,9], flash point and stability against oxidation. But, the use of

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PC is limited if graphite negative electrode materials with a high degree of graphitisation are used. This limitation is ascribed by Besenhard et al. to a phenomenon called solvent co-intercalation, causing graphite exfoliation, i.e., destruction of the crystal lattice [3,8]. Particularly in the first charge cycle, before the formation of the protective SEI film on Li_xC_6 is finished, the tendency for solvent co-intercalation is high [9]. The exfoliation is finally stopped by the formation of a protecting SEI film. Aurbach et al. [10,11] suggested that in PC solutions graphite particles crack due to gas formation on the graphite surface and within existing surface cavities. The graphite anodes are thus “deactivated” due to electrical isolation of the cracked particles by surface films.

The influence of the electrolyte system on the exfoliation process has been studied in several publications, but still little is known about the influence of the particular solvent components on the solvent co-intercalation process, which seems to be responsible for the graphite exfoliation process that can be observed in the case of some graphite materials [12–15]. Besides the electrolyte system, the graphite material properties also influence the graphite passivation process. The critical material parameters reported are the surface chemistry and morphology, the ratio of basal planes to edge planes, particle size distribution, the ratio of rhombohedral and hexagonal phase in the graphite crystal structure and the existence of a certain disorder on the particle surface [14,16,17]. Careful investigation of all the factors which play a crucial role for the graphite passivation or graphite exfoliation, as well as their interaction should give a clearer picture of the complexity of the SEI layer composition and the SEI formation mechanism.

In this paper, a systematic study of the first electrochemical intercalation of lithium into several synthetic and natural graphites in EC/DMC and EC/PC mixtures containing 1 M $LiPF_6$ is presented. The passivation process of these graphite materials is compared by several in situ and ex situ methods and correlated with the graphite material bulk and surface properties.

2. Experimental

Different types of TIMREX® (TIMCAL SA, Bodio, Switzerland) graphite materials were used as negative electrode materials. Synthetic (SFG, KS) as well as natural (E-LSG) graphite material were applied as received [18]. The samples have particle sizes (d_{90}) varying from 4 to 75 μm. The number in the graphite designation indicates the d_{90} particle size value. For example, in samples with the number 6 (SFG6, KS6 and E-LSG6) 90% of the particles are smaller than 6 μm. The basic parameters of all samples are summarised in Table 1. For the determination of the specific BET surface area, nitrogen gas adsorption measurements were performed at 77 K using a Micromeritics ASAP2010. The particle size distribution was determined by laser diffraction (MALVERN Mastersizer).

The crystallinity of the graphite materials was characterised by X-ray diffraction (XRD) measurements with a STOE Stadip diffractometer in Debye–Scherrer geometry using monochromatic Cu Kα_1 radiation (1.5418 Å). The average crystallite size along the crystallographic *c*-axis (L_c) and the *a*-axis directions (L_a) were determined from the FWHM of the carbon (0 0 2) and (1 0 0) Bragg reflexes, respectively, after correction by the factor for the instrumental broadening [19]. The rhombohedral fraction (3R phase) was derived by the comparison of the intensities of the (1 0 1) hexagonal and rhombohedral diffraction peaks.

Table 1
Structural bulk parameters, surface properties and results of the electrochemical charge/discharge measurements (1st cycle irreversible charge losses) of different TIMREX® graphites in 1 M $LiPF_6$, EC/DMC and EC/PC electrolyte

Graphite	BET ($m^2 g^{-1}$)	d_{50}[a] (μm)	Rhombohedral 3R-phase[b] (%)	L_c (Å) [XRD]	L_a (Å) [XRD]	L_a (Å)[Raman]	Irreversible charge loss [1st cycle] (%)	
							EC/DMC	EC/PC
SFG6	17.1	3.3	37	303	622	240	20	19
SFG10	10.4	6.7	29	360	565	630	17	57
SFG15	8.8	9.1	23	365	609	760	12	62
SFG44	4.6	23.9	17	401	572	530	7.2	87
SFG75	3.3	29.0	16	399	597	680	6.5	89
KS4	19.4	3.6	40	205	345	200	30	34
KS6	13.8	5.6	29	275	475	210	24	65.2
KS10	12.3	7.5	19	305	613	620	21.5	80.5
KS15	12.0	8.2	25	297	520	460	20	82
KS44	6.2	20.0	12	313	557	390	13	88.5
KS75	3.0	24.0	11	336	543	450	11	91
E-LSG6	14.2	3.5	41	335	507	340	18	19
E-LSG15	8.5	8.9	29	353	566	620	14.2	14
E-LSG44	4.5	22.9	21	405	600	420	8.4	81

Structural bulk parameters of graphite were obtained from X-ray diffraction measurements. The particle size distribution of the graphite was determined by laser diffraction (MALVERN Mastersizer). Surface properties: listed specific BET surface areas were obtained from nitrogen adsorption measurements, and Raman spectroscopy was used to characterise the crystallinity in the surface-near regions of the graphite particles (L_a-values).

[a] For example, in sample SFG6, 50% of the particles are smaller than 3.3 μm.

[b] Fraction of the rhombohedral phase (3R) in graphite.