Electrochemical intercalation of lithium into carbons using a solid polymer electrolyte

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Abstract

A study of the electrochemical performance of carbon materials from different types was carried out on true solid polymer-based poly(ethylene oxide) (PEO) with LiTFSI for application as the negative electrode in lithium ion solid-state batteries (LISSBs) at 60 °C. The reversible and irreversible capacity depend strongly on the crystallinity, the form of carbon and the impurities. A comparison of particle versus fiber was done when we investigated the charge/discharge characteristics with different current densities. The galvanostatic curves show high reversibility of the lithium–carbon in solid polymer electrolyte. The kinetics of electrochemical intercalation of lithium into carbon was studied by impedance spectroscopy especially for evaluating the diffusion coefficient in different origins of carbon. The degree of ionization of lithium was investigated by using solid-state ^7Li nuclear magnetic resonance spectroscopy when the electrode is fully intercalated or doped down to 0 V. The chemical shift of ^7Li NMR in lithium intercalation or doping in the carbons was classified in two ranges, 42 ppm and 9 ppm. ^7Li NMR suggests the carbon with a 42 ppm range is the best choice for LISSBs. © 1997 Elsevier Science S.A.

Keywords Lithium, Intercalation, Carbon; Solid polymer electrolytes

1. Introduction

A primary objective of this current research is a contribution to the safety problem due to growth of lithium dendrites during cycling. Carbon materials are now generally accepted as excellent alternatives for lithium metal as the anodes in lithium batteries. However, the low coulombic efficiency observed for the electrochemical intercalation of lithium ions in carbon materials is delaying the commercialization of these 'rocking-chair' [1] or Li-ion batteries [2].

AA-size batteries with a liquid electrolyte for electronic applications have been found to be relatively safe [3] but for large batteries, in particular those using a large amount of liquid electrolyte, gas will appear when the electrolyte decomposes due to the destruction of the protective layer at the carbon surface. Decomposition may also occur at voltages exceeding 4 V. Safety will therefore be a major issue at scaling-up. For this reason, it is essential that large-scale Li-ion batteries use a pure solid polymer electrolyte with no added liquid solvent and no significant vapor pressure.

In the literature [4,5], the use of a carbon electrode has been demonstrated using a solid polymer electrolyte based on poly(ethylene oxide) (PEO) and PEO–poly(propylene oxide) (PPO) at 80 °C. In this paper, in order to form the electrodes we combined three different types of carbonaceous materials: (i) a 0D structure composed of mesocarbon micro-beads (MCMB); (ii) a 1D structure composed of carbon fibre ex-mesophase (MPCF), and (iii) a 2D structure composed of natural graphite (NG). Each form was added to a solid polymer electrolyte at 60 °C. Cells were made in the laboratory in order to determine the irreversibility and reversibility of the electrode reaction. The effect of structure and carbon surface will be discussed. The state of lithium in carbon when fully intercalated was demonstrated by ^7Li NMR. The diffusion coefficient of lithium in the three types of carbon was determined by impedance spectroscopy.

2. Experimental

The sources for the various forms of carbon in this study were: natural graphite (NG-7), 7 μm in particle size with 99.99 purity (NG7A), 99.5 (NG7B) from Kansai Coke and Petrochemicals, well graphitized MELBLON carbon fibres from Petoca; two sources of MCMBs were used, one from Osaka Gas Company, treated at 2800 °C and coded as MCMB28-OG, the second from Kawasaki Steel Company,
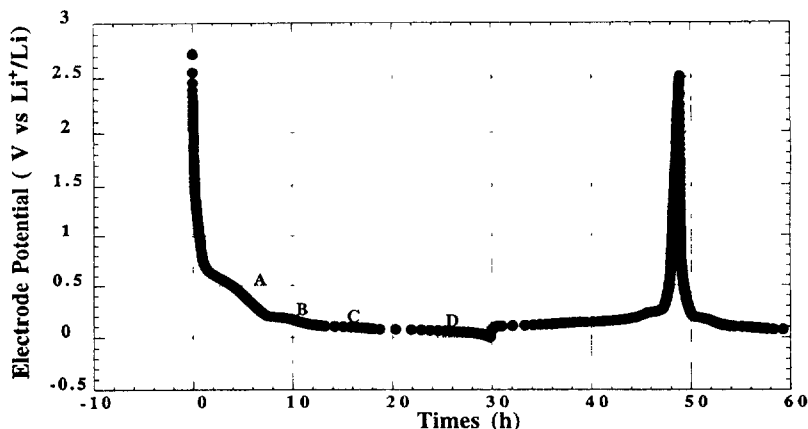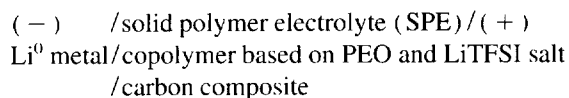
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Fig 1 Galvanostatic (C/15), discharge/charge curves obtained with NG7A/SPE/Li at 60 °C.

treated at 700 and 2800 °C and coded, respectively, as MCMB7-KA and MCMB28-KA.

The discharge (intercalation)/charge (de-intercalation) cycling for the carbon electrode was carried out using two electrode cells with lithium metal. The initial cell chemistry for the negative electrode is based on

(–)   /solid polymer electrolyte (SPE)/(+)
Li^0 metal/copolymer based on PEO and LiTFSI salt
        /carbon composite

The carbon working electrode was prepared by adding 50% by volume to SPE and coating on a copper foil by the doctor blade method. The electrode was dried under vacuum at 85 °C for 24 h before use. The discharge/charge cycles for this electrode were carried out using the galvanostatic method (Macpile® Biologic, Claix, France) at 24 mA/g (C/15) to measure the exact charge/discharge in the range of 0 to 2.5 V. The impedance measurement and diffusion coefficient was described elsewhere [5]. For the nuclear magnetic resonance (NMR) study, an electrode discharged to 0 V was taken from the cell and was introduced in an NMR tube (5 mm in diameter and 25 mm in length) and set into a wide-line probe of a solid-state ^{7}LiNMR spectrometer (Chenagnetics); LiCl was used as an external standard. In the case of study of the

film passivation (500 mV), the electrode must be salt-(LiTFSI) free. All experiments were performed at 60 °C.

3. Results and discussion

Fig. 1 shows the discharge (intercalation)/charge (de-intercalation) cycle obtained with NG7A at a C/15 rate. The discharge/charge curve shows one irreversible plateau (A) at 500 mV and three reversible plateaus (B, C and D) at 160, 75 and 50 mV, respectively. The irreversible plateau is due in part to the formation of a passivation layer [6]. The reversible plateaus are due to the staging phenomenon [6] of graphite intercalation compounds (GICs). The effect of impurity was demonstrated in Fig. 2; in the case of NG7A, the first charge at 372 mAh/g is reproducible and not modified by any subsequent charge/discharge cycle. For NG7B, the reversible capacity decreases dramatically with cycle number, possibly because the impurity affects the chemistry of the passivation layer (PL) as well as its ionic diffusivity. The metallic impurities diffusing from the SPE, may affect the chemistry of the PL. After purification, the graphite surface is modified to produce a good PL. The first coulombic efficiency (1CE) was found to be 66% and is lower than that from liquid electrolytes (92%), which has a higher recovery

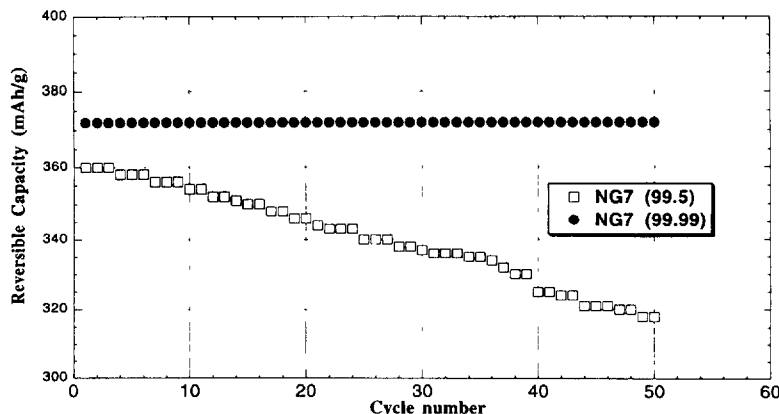Fig 2 Effect of the impurities of natural graphite on the cycleability

Table 1
Electrochemical and structure characteristics of carbons used for this study

|	1st discharge (mAh/g)	1st charge (mAh/g)	1st CE (%)	10th discharge (mAh/g)	10th charge (mAh/g)	10th CE (%)	Structure	Voltage profile	D (cm^2/s) $x = 0.1$	D (cm^2/s) $x = 0.5$	Chemical shift (ppm)
NG7A	563	372	66	372	372	100	Ordered layer	Flat	3.2×10^{-5}	1×10^{-9}	42
MELBLON	430	301	70	300	300	100	Ordered layer	Flat	6.3×10^{-7}	4×10^{-9}	41
MCMB28-OG	506	294	58	292	292	100	Ordered layer	Flat	1.6×10^{-7}	3×10^{-8}	43
MCM28-KA	514	293	57	290	290	100	Ordered layer	Flat	2×10^{-7}	2.5×10^{-8}	43
MCMB7-KA	976	516	42	160	155	97	Disordered	Sloping	6.3×10^{-8}	2.5×10^{-9}	9
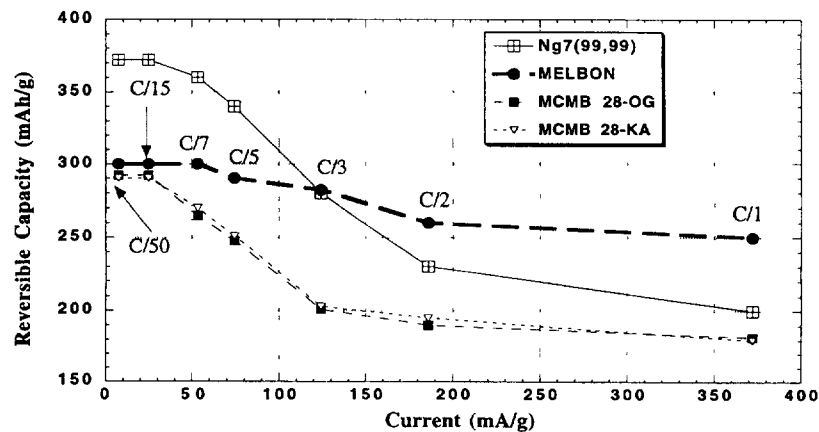
Fig. 3. Current density vs. reversible capacity at 60 °C.

yet a better wetting of the graphite surface. The highest 1CE (70%) was found with MELBLON (Table 1), which has a different orientation, ensuring good contact. These fibres look like fabric and may reach a high specific surface area. The lowest 1CE, found with MCMB7-KA, is due to the low crystallinity [7] as well as the presence of heteroatoms (H, O) on the surface of the MCMB. However, this product had the highest first charge, although the capacity decreased with increasing the cycle number.

The NG7A shows the highest reversible capacity (Table 1), namely 372 mAh/g. MELBLON gives 300 mAh/ g. Not surprisingly, MCMB28-OG and MCMB28-KA have the same reversible capacity, about 290 mAh/g, since they were both treated at 2800 °C. The reversible capacity of carbon materials is thus directly related to their crystallinity.

A study was undertaken of the direct state of lithium in these three different carbon materials by ^{7}Li NMR, when the electrode was fully intercalated (discharged at 0 V). Two groups were found: a 42 ppm group of highly graphitized carbon materials (NG7, MELBLON, MCMB28-CA, MCMB28-KA, characteristic of first stage GIC [5]) and a 9 ppm group of low graphitized carbon materials (MCMB7-KA). In the latter case, the lithium is considered as ionic [7]. No lithium metal (260 ppm) was detected even in MCMB7-KA (high capacity: first discharge).

The d.c. of lithium into carbon (Table 1) was determined at two different rates ($x = 0.1, x = 0.5$) in Li$_x$C$_6$. A large range of d.c. values was found for MELBLON. Fig. 3 shows the effect of current density versus reversible capacity. At high

rate ($C/1$), carbon fibres present the highest capacity; thus, at rapid charge/discharge rates, fibres are a better choice than particles for use as the negative electrode in Li-ion batteries.

4. Conclusions

By varying the nature of carbon, the highest capacity at $C/$ 15 is found with NG7A (99.99). The highest 1CE so far reported (70%) is obtained with MELBLON. There is a clear relationship between impurity and cyclability. The diffusion coefficient is greater when we used carbon fiber-HTT (heat-treatment temperature). The study of ^{7}Li NMR suggests that the carbon HTT (≥ 2800 °C) is the best choice for LISSBs. According to this view, industrial LISSBs using SPE is a safe alternative to liquid-based systems for large-scale electric vehicle batteries, hybrid-traction vehicles or space applications.

Acknowledgements

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