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High capacity hard carbon anodes for sodium ion batteries in additive free electrolyte

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ABSTRACT

Electrochemical performance of hard carbon prepared from sugar pyrolysis was investigated against sodium anodes. Specific surface area and graphitization degree are determinant for achieving the highest reversible capacity ever reported (more than 300 mAh/g at C/10 after 120 cycles) with excellent rate capability. Such results were obtained using additive free EC:PC based electrolyte which appears to induce the formation of a more conducting solid electrolyte interphase (SEI) than that produced in the presence of 2% fluoroethylene carbonate (FEC).

1. Introduction

The development of negative electrodes based on carbonaceous materials was the key for the commercial implementation of the Li-ion battery technology [1,2], enhanced performance being achieved through electrolyte formulation (e.g. preventing graphite exfoliation through formation of a stable SEI layer in ethylene carbonate (EC) containing electrolytes [3]).

The feasibility of an analogous room temperature Na-ion technology is especially attractive [4–6] for large scale applications where cost and raw materials supply is a must. Within this scenario, and in spite of alternative materials being developed [7], carbonaceous anodes remain appealing for their low cost and availability. After preliminary reports [8,9] of poor performance, recent progresses have been made in terms of capacity and reversibility using commercial hard carbons [10,11] not specifically developed for Na-ion batteries. Prompted by such findings, we decided to ascertain whether enhanced performance could be achieved. We embarked on a study based on the early work by Dahn and co-workers which allowed tuning the hard carbon microstructure and performance in Li-ion cells through the control of pyrolysis temperature for its preparation [12]. We investigated both the effect of milling [13] and of electrode processing atmosphere which can affect microstructure and surface chemistry, respectively. Finally, the possible benefit of using electrolyte additives, such as fluoroethylene carbonate (FEC) [9] was also evaluated.

2. Experimental

Hard carbon was made as described in [12] by pyrolysis of sugar at 1100 °C (6 h, argon flow), HC thereafter. Samples prepared under fluxes <100 cm^3/min exhibited poor electrochemical performance against sodium anodes, in agreement with parallel findings on lithium cells [12], and results will not be reported here. The as prepared hard carbon was further ball milled (PM100 Retsch Miller, stainless steel container, 3 stainless steel balls, 500 rpm, 2 h) and heat treated again at 1100 °C (6 h, argon flow), PBMHC thereafter.

Raman spectra were recorded using a LabRam HR800 system in backscattering geometry, using for excitation the 632.5 nm line of a He–Ne laser, which was focused on the sample to a spot of around 2 μm in diameter. BET surface area measurements were done using an ASAP 2000Micromeritics instrument. X-ray powder diffraction (XRD) was performed on a Siemens D5000 with Cu Kα radiation source (0.15418 nm). Scanning Electron Microscopy (SEM) studies were performed using a Quanta 200 ESEM FEG FEI microscope. DSC measurements were done on a DSC 204F1 Netzsch calorimeter, following a protocol described elsewhere [14].

Composite electrodes mimicking industrial technologies were prepared from slurries (90 wt.% active material, 5 wt.% of Polyvinylidene fluoride binder (PVDF, Arkema) and 5 wt.% of Super P carbon (Csp hereafter from Timcal) in N-Methylpyrrolidone (NMP, Aldrich)) containing either HC or PBMHC [14]. Mixing was performed under air or argon atmosphere using a PM100 Retsch planetary Ball Miller.

Cycling experiments were performed in two-electrode Swagelok cells in galvanostatic mode with potential limitation (GCPL) at different rates ranging from C/10 to 2C (1C being one Na^+ inserted in 1 h) to monitor capacity evolution upon cycling. A 1 M $NaClO_4$ solution in EC

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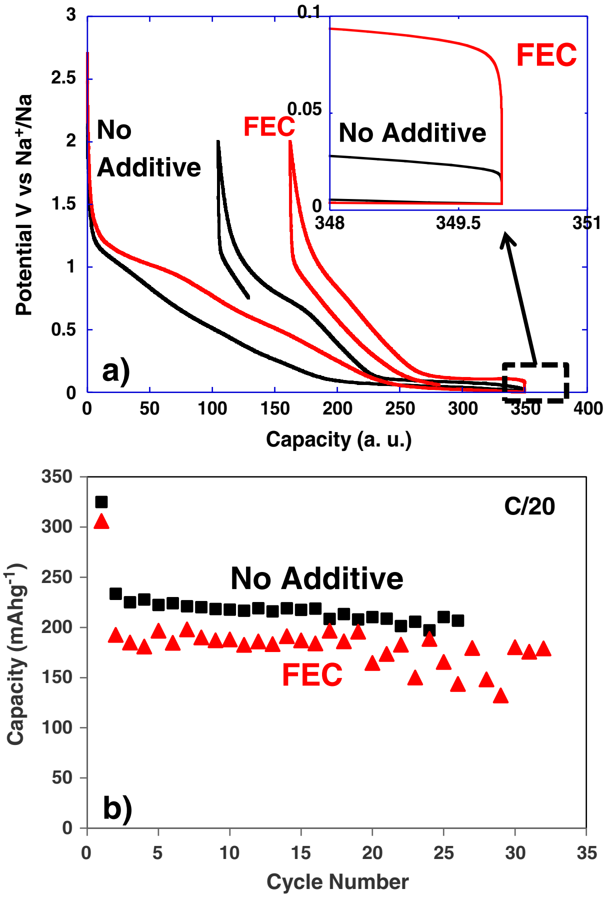

Fig. 1. a) First cycle potential versus normalized capacity profiles and b) discharge capacity vs. cycle number for hard carbon electrodes cycled (C/10) in 1 M $NaClO_4$ in EC:PC with (red curve) or without (black curve) FEC addition.

(Aldrich, 99.0%) and propylene carbonate (PC) (Aldrich, 99.7%) mixture (1:1 in weight) with or without FEC additive (2 vol.%, Solvay) was used as electrolyte. The water content in all as prepared electrolytes was found to be <50 ppm (Karl-fisher titration). All electrochemical tests were performed using a Bio-Logic VMP3 potentiostat assembling twin cells to ensure reproducibility of results. Electrochemical Impedance Spectroscopy (EIS) measurements (10 mV perturbation amplitudes, 1000 kHz–50 mHz) were performed in three electrode Swagelok cells after a 2 h OCP period.

3. Results and discussion

After our recent study demonstrating that EC:PC based electrolyte allows the building of an electrochemically and thermally stable SEI layer on hard carbon [14], we investigated the effect of FEC addition. Indeed, when present in small amounts (2%), benefits in terms of cyclability for hard carbon in coin cells with PC electrolytes have been reported [11] to the expense of a somewhat lower capacity for the first cycle. Fig. 1a exhibits the voltage versus normalized capacity profiles of hard carbon electrodes cycled in $NaClO_4$ in EC:PC electrolytes without (black curve) or with 2% FEC (red curve). In the present case, FEC induces a significant coulombic efficiency decrease and an increase of the overpotential between charge and discharge (cf. inset of Fig. 1a). Such an effect is detrimental to the reversible specific capacity since it prevents fully accessing the low potential plateau (at ca. 0.1 V vs Na^+/Na, Fig. 1b). Thus the SEI promoted by FEC (polymerizing agent) seems to exhibit much poorer conductivity than that formed in EC:PC mixtures without any additive, which is probably the reason why amounts of FEC larger than 2% were found to have detrimental effects [11]. In view of such results, the electrochemical performances of HC electrodes were evaluated in additive free $NaClO_4$ in EC:PC electrolytes.

Characterization of HC and PBMHC was performed by means of Raman spectroscopy, X-ray diffraction and BET surface area measurements. Raman spectra (cf. Fig. 2d) exhibit two broad bands at about 1330 and 1595 cm^{-1} (the defect-induced D band and the crystalline graphite G band of carbon) with integrated intensity D/G ratios of ca. 2.6 and 2.1 for HC and PBMHC respectively. Since this ratio allows for an evaluation of the degree of graphitization [15], it seems straightforward to conclude that it is higher for PBMHC (smaller D/G ratio). This is also in agreement with XRD patterns, since a sharper (002) peak is observed for PBMHC (cf. Fig. 2e), d_{002} lattice spacings being 0.387 and 0.343 nm for HC and PBMCH respectively. Finally, BET measurements (cf. Fig. 2c) point at a much larger specific surface area with slightly larger average pore size for PBMHC (ca. 135 m^2/g and 3.7 nm) than HC (ca. 24 m^2/g and 2.9 nm).

Fig. 3a depicts the first cycle voltage versus capacity profile for HC, and PBMHC electrodes processed under air or argon. No significant difference was observed between slurries prepared under air (dashed curves) or under argon (solid curves). This strongly suggests that the surface chemistry is either not modified using different mixing atmosphere or it has no significant impact on the electrolyte decomposition/SEI formation. The overall capacities observed upon first reduction are similar (540 mAh/g for HC and 505 mAh/g for PBMHC) but significant differences exist in the coulombic efficiency (ca. 61% and 41% respectively). This is easily understandable from the higher BET area for PBMHC resulting in a larger surface of hard carbon in contact with the electrolyte and therefore a larger amount of SEI layer and in agreement with tape casted electrodes (cf. Fig. 2a and b) containing larger particle sizes for HC when compared to PBMHC. (Note that, as expected, changes in mixing atmosphere do not have any influence on particle size). DSC investigations (not shown) are consistent with such findings, since a larger amount of heat is generated (1102 J/g) for fully sodiated PBHMC electrodes than for HC (920 J/g), which in turn points at the safety benefits of using low specific surface area hard carbon anodes.

Stable capacities of about 210 and >300 mAh/g were respectively recorded for PBMHC and HC based electrodes at C/10 and after more than 60 cycles (cf. Fig. 3c), with coulombic efficiencies of ca. 96% and 99.9% respectively. The performance of HC upon sustained cycling is, to the best of our knowledge, the best reported to date. This is somewhat surprising since larger capacities would a priori be expected for smaller particles (i.e. PBMHC). However, soft carbons with d_{002} values around 0.344 nm were previously reported to exhibit poor performances in lithium cells [16]. For comparison Cao et al. [17] and Tang et al. [18] recently reported reversible capacities of about ca. 250 and 160 mAh/g, respectively, with hard carbons with d_{002} lattice spacings of ca. 0.37 and 0.401 nm. The overpotential at the end of each cell reduction was systematically evaluated (cf. inset in Fig. 3a) to ascertain whether an enhanced resistivity could prevent accessing the full capacity of PBMHC at low potentials [14] but very small differences were observed with HC. Results of EIS measurements before cycling (Fig. 2b) indicate that the charge transfer resistance (cf. lower inset in Fig. 2b) seems slightly larger for PBMHC electrodes regardless of the mixing atmosphere, but values converge quickly upon cycling. From the corresponding Bode diagram (upper insert in Fig. 3b), significant differences can be seen in the low frequency region of the curves being shifted to lower frequencies for PBMHC electrodes, which suggests a hindered diffusion of Na^+ through the electrode [19,20] but once again values converge upon cycling. Overall, the differences between the specific reversible capacities for PBMHC and HC cannot be related to either differences in overpotential, charge transfer resistance or Na^+ diffusion, which clearly points at the graphitization degree as main determinant feature. Indeed, it is well known that graphitic carbon exhibits very poor reversible capacity when cycled against sodium anodes [9].