



Short communication

# On the high and low temperature performances of Na-ion battery materials: Hard carbon as a case study

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## ABSTRACT

Electrochemical performance of hard carbon (HC) prepared from sugar pyrolysis was investigated against sodium anodes at temperatures ranging from  $-15\text{ }^{\circ}\text{C}$  up to  $75\text{ }^{\circ}\text{C}$ . Carbon coating was performed on HC decreasing its surface area and allowing significant improvement in terms of the first cycle coulombic efficiency and thus, irreversible capacity loss. Electrochemical performances of HC at various temperatures pointed at the IR drop of the cell being determinant for achieving the highest reversible capacity ( $450\text{ mAh/g}$  at C/10,  $75\text{ }^{\circ}\text{C}$ ) and rate capability ( $340\text{ mAh/g}$  at 2C,  $75\text{ }^{\circ}\text{C}$ ) ever reported. Stable cycling was also achieved at  $-15\text{ }^{\circ}\text{C}$  with reversible capacity of ca.  $265\text{ mAh/g}$ .

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## 1. Introduction

Research on sodium-ion battery (SIB) materials has recently boosted within the scientific community, as sodium resources are “unlimited”, attainable at low cost, and geographically distributed [1–4]. As graphite does unfortunately not significantly insert sodium ions [5–7], hard carbon (HC hereafter) is currently the only practical negative electrode active material. Its main drawback is the high irreversible capacity upon the first cycle, well known also in Li-ion cells, which has important implications for cell balancing. This phenomenon is commonly related to surface reactivity with the electrolyte and thus we have attempted to reduce it through coating. For this, instead of using chemical vapor deposition (CVD) to apply a carbon coating, as commonly done to improve performance of graphite anodes [8], we developed a simpler physical method, enabling conformal uniform particle coating [9,10].

After mitigation of the first cycle irreversible capacity loss, we became interested on the thermal dependence of HC electrochemical performance which has, to the best of our knowledge, not been reported to date. The impressive thermal stability window of electrolytes based on a mixture of ethylene carbonate (EC) and propylene carbonate (PC) (vitreous transition for temperatures near  $-95\text{ }^{\circ}\text{C}$  and a single exothermic peak around  $240\text{ }^{\circ}\text{C}$  in the DSC curves) [11] prompted us to undertake a systematic study on the electrochemical performances of HC electrodes tested at various

temperatures ranging from  $-15\text{ }^{\circ}\text{C}$  up to  $75\text{ }^{\circ}\text{C}$ . The results achieved shed new lights on the origin of the poor rate capability exhibited by HC electrodes.

## 2. Experimental

HC was prepared as described in [12] by pyrolysis of sugar at  $1100\text{ }^{\circ}\text{C}$  for 6 h under argon flow. Carbon coating of the HC was performed as reported in Ponrouch et al. [9]. Briefly, it involves a physical vapor deposition of carbon onto a powder that is agitated throughout the deposition process which leads to uniform coating (ca. 2 nm thick). BET surface area of uncoated and carbon coated HC powder were measured using an ASAP 2000 Micromeritics instrument. Scanning Electron Microscopy (SEM) studies were performed using a Quanta 200 ESEM FEG FEI microscope.

Composite electrodes were prepared from slurries (90 wt.% HC carbon coated or uncoated, 5 wt.% of Polyvinylidene fluoride binder (Arkema) and 5 wt.% of Super P carbon (Timcal) in N-Methylpyrrolidone (Aldrich)) [11].

Electrochemical tests were performed using a Bio-Logic VMP3 potentiostat in two-electrode Swagelok cells in galvanostatic mode with potential limitation (GCPL) at different rates ranging from C/10 to 2C (1C being one  $\text{Na}^+$  inserted in 1 h) to monitor capacity evolution upon cycling. Twin cells were assembled in all cases to ensure reproducibility of results. The electrolytes consist of 1 M  $\text{NaPF}_6$  solution in EC (Aldrich anhydrous 99.0%) and PC (Aldrich anhydrous 99.7%) mixture (1:1 in weight) with or without addition of 10 wt.% of dimethyl carbonate (DMC, Aldrich

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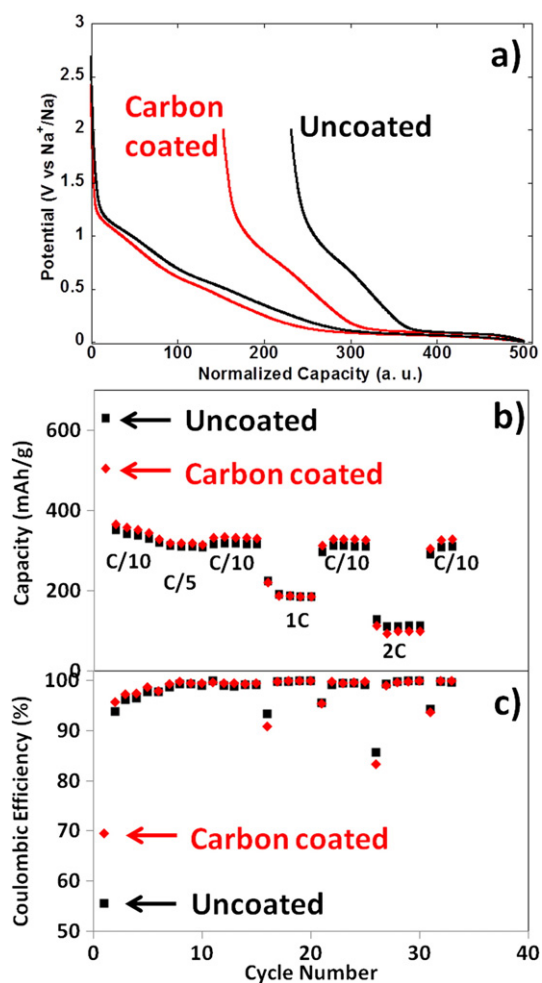
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anhydrous 99.0%) [11,13]. The water content in all electrolytes was measured by Karl-fischer titration and found to be lower than 50 ppm in all cases.

### 3. Results and discussion

The effect of carbon coating on surface area was investigated by BET measurements. Results on uncoated (ca. 95 m<sup>2</sup>/g) and carbon coated HC (ca. 70 m<sup>2</sup>/g) powders demonstrate a decrease in surface area after coating. This induces a significant improvement in terms of coulombic efficiency upon the first cycle with 70% and 55% being recorded for carbon coated and uncoated HC, respectively (Fig. 1a and c). The cycling performances were found to be very similar (Fig. 1b and c) in both cases in terms of i) reversible capacity (ca. 325 mAh/g at C/10), ii) rate capability (ca. 110 mAh/g at 2C) or iii) coulombic efficiency (higher than 99% after 5 cycles). Such findings clearly demonstrate that the main reason behind the first cycle irreversible capacity loss is surface reactivity, and thus, it can be expected that further improvements can take place by its modification using alternative techniques. Given the simplicity of the physical carbon coating procedure and its beneficial effect, it was adopted as part of our standard electrode preparation protocol.

The electrochemical performances of carbon coated HC were firstly evaluated at temperatures ranging from 25 °C to 75 °C (higher temperatures were not considered due to the low melting point of



**Fig. 1.** a) First cycle voltage versus normalized capacity profiles for electrodes prepared with carbon coated (red) and uncoated (black) hard carbon cycled at 25 °C in 1 M NaPF<sub>6</sub> in EC<sub>0.5</sub>:PC<sub>0.5</sub> based electrolytes (recorded at C/10). b) Discharge capacity and c) coulombic efficiency versus cycle number.

Na, ca. 97.7 °C). Fig. 2a exhibits the voltage versus capacity profiles (first cycle) of carbon coated HC electrodes cycled in 1 M NaPF<sub>6</sub> in EC<sub>0.5</sub>:PC<sub>0.5</sub> electrolytes at 25 °C (black curve) or 75 °C (red curve). Upon the first reduction higher capacity (ca. 850 mAh/g) is recorded at 75 °C when compared to 25 °C (ca. 500 mAh/g). Although, the first cycle coulombic efficiency is lower at 75 °C (50%) than at 25 °C (70%, Fig. 2a and d), a significantly higher reversible capacity is recorded upon cycling at C/10: ca. 420 mAh/g at 75 °C and ca. 325 mAh/g at 25 °C with similar coulombic efficiencies (higher than 99% after 5 cycles, see Fig. 2b and d). Typical SEM micrographs of the carbon coated electrodes cycled at 75 °C presented in Fig. 2 are similar to those of fresh electrode before cycling (Fig. 3) indicating that neither significant modification of the microstructure nor significant decomposition of the electrolyte on the surface of the electrodes takes place. High rate capability is also achieved at 75 °C and capacity as high as ca. 273 mAh/g is measured at 2C (Fig. 2b). Similar results are obtained at 75 °C if 10 wt.% of DMC is added to the electrolyte (data not shown for sake of clarity) with slightly better reversible capacity (ca. 450 mAh/g at C/10) and improved rate capability (ca. 340 mAh/g at 2C). Such reversible capacity and rate capability values recorded at 75 °C are the best reported so far for HC electrodes. While the reason behind this significant improvement of performances of HC electrodes at 75 °C remains to be further studied, our results prove that it is, at least partly, related to the smaller IR drop measured at this temperature. Indeed, large IR drops prevent from accessing a significant part of the electrochemical capacity for hard C, since it is related to a plateau at very low potential [11]. IR drop values recorded at 75 °C and C/10 (see inset in Fig. 2c) stabilize after five cycles at values as low as 5 mV while 45 mV is measured at 25 °C. This difference is emphasized at 1C with an IR drop of 40 mV and 115 mV, respectively, at 75 °C and 25 °C, which can explain the excellent rate capability of HC electrodes at 75 °C. When 10 wt.% of DMC is added to the electrolyte the IR drop at 1C is as low as 8 mV at 75 °C. In contrast to suggestion that Na insertion into HC is kinetically limited while Na<sup>+</sup> extraction is very fast [14], the excellent rate capability recorded at 75 °C using the same charge and discharge rates demonstrates that both are fast processes and points at the main limiting factor for high rate capability being the total cell IR drop. This is also most probably behind the lower reversible capacity recorded for HC against sodium anodes when compared to lithium metal, [15] which would be related to the 0.3 V lower standard reduction potential difference between sodium and lithium metal. It is also worth mentioning that an additional redox process seems to occur at 75 °C upon oxidation (see red arrow in Fig. 2a), which is still under study. Although the nature of this process is still unclear it has been observed to be rate dependent and to have limited kinetics, as it tends to disappear at high C rates (Fig. 2c).

The performances of carbon coated HC were also evaluated at temperatures ranging from −15 °C to 25 °C. Fig. 4a exhibits the voltage versus capacity profiles of a carbon coated HC electrode cycled in 1 M NaPF<sub>6</sub> in EC<sub>0.45</sub>:PC<sub>0.45</sub>:DMC<sub>0.1</sub> at 25 °C (black curve), 0 °C (red curve) and −15 °C (blue curve). Given the non-negligible IR drop recorded at −15 °C (ca. 100 mV, inset in Fig. 4a) the capacity upon reduction is less than 130 mAh/g with a 3 mV vs. Na<sup>+</sup>/Na potential cut off. Therefore, the lower cutoff voltage has been fixed at 3, −15 and −80 mV vs. Na<sup>+</sup>/Na for temperatures of, respectively, 25 °C, 0 °C and −15 °C, with sodium plating not being observed in any of such conditions. The reversible capacity recorded upon cycling at 0 °C (ca. 260 mAh/g) and −15 °C (ca. 265 mAh/g) at C/10 is very similar to the one achieved at 25 °C (ca. 290 mAh/g) and in all cases the coulombic efficiency was found to be higher than 99% (Fig. 4b and c). The fact that our electrolyte formulation allows so high capacity retention for an active material cycled at such low temperature is encouraging for practical application of Na-ion batteries.

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