Peculiar Li-storage mechanism at graphene edges in turbostratic carbon black and their application in high energy Li-ion capacitor

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GRAPHICAL ABSTRACT
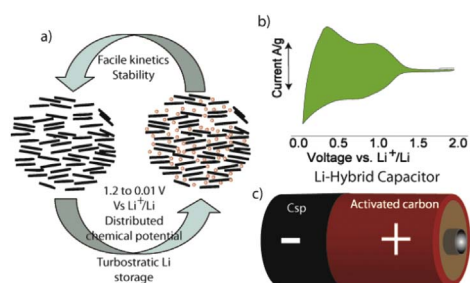
ABSTRACT

We report experimental evidence for the specific Li-storage at turbostratic graphene edges of a well-known and cheap Super P® carbon black (Csp) material, which is usually used as a conductive additive in composite electrodes. Indeed, *operando* XRD and HR-TEM consistently demonstrate Li insertion occurs with zero expansion of graphene layer up to a composition of $Li_{0.4}C_6$ (150 mA h/g) that is reached at 0.01 V *vs.* Li^+/Li. ^7Li NMR substantiates these results and suggests that the weak electronic transfer from the carbon host to the intercalant could help local reorganization of the layer order as suggested by the unexpected reversible changes of the (002) Bragg peak intensity during the charge-discharge process. Our observations also indicate this insertion mechanism is kinetically favored resulting in remarkable cycling stability over 1000 cycles and power capability allowing to sustain 110 mA h/g at 8 A/g (21 C) in half cell. The capability of Csp as an efficient anode is ultimately demonstrated in a lithium hybrid capacitor against a positive electrode of activated carbon. The full cell delivers a maximum energy of 120 Wh/kg (4.3–2 V) and remarkable capacity retention over 1800 cycles.

1. Introduction

Electrochemical storage systems [1] with concomitantly high energy and power capabilities are the ideal systems for future applications including electric vehicles. Li-ion (LiB) batteries deliver high specific energy densities (150–200 Wh/kg) however, at the expense of low power performance (1–3 kW/kg) due to poor ionic transport in the electrode porosity [2] [3]. The opposite holds for electrochemical capacitors (5 Wh/kg and 10 kW/kg) for which electrochemical reactions are confined at the surface [4] [5]. One of the routes to enhance the power characteristic of LiB is to reduce the ionic diffusion paths *via* downsizing the grains of the active material. However, this strategy

hampers the electrical conductivity and volumetric density. Another approach consists in coupling a supercapacitor electrode to a LiB into a so-called Lithium-ion capacitor (LICs) [6], [7]. The later possesses power capabilities and cycle life approaching that of supercapacitor without greatly compromising the energy density. In LICs, the negative electrode store Li through various chemistries such as insertion ($Li_4Ti_5O_{12}$ (LTO) [8], graphite [9] etc.), alloying (Si, Sn etc.) or conversion (M_aX_b, M = transition metal, X = O, S, F, P, N …) [10], [11]. The capacity is balanced at the positive electrode by double layer charge storage using high surface area supercapacitor grade carbon. Such systems show improved energy density, compared to the pure supercapacitor, thanks to the high Li storage capacity and a low average potential (< 1 V $vs.$ Li^+/Li) of the negative electrode. However, due to poor kinetics and large volume variations associated with the Li insertion, alloying or conversion mechanisms, power and cycle life performance of the negative electrode are the bottleneck of LIC device performance [12]. Focusing on carbon materials and especially graphite, intercalated Li between graphene layers are in the quasi-metal state ($Li_{0.1}^+$ in LiC_6) [13]. The corresponding Li diffusion is associated with an activation energy of approx. Ea = 0.5 eV [14] that participates in hindering the overall intercalation kinetics. Other Li uptake mechanisms into various different carbons such as H-terminated carbon, micropores, turbostratic edges etc., have been described [15]. Hydrogen-containing carbons, although they have a high specific capacity, show large potential hysteresis arising from the quasi-reversible binding of lithium on the hydrogen-terminated edges [15] [16]. Such large hysteresis is also observed in micro-pores carbon [17]. Based on a theoretical study, Barone et al. have proved that the activation energy of edge sites in graphene is 0.15 eV smaller than that corresponding to the surface [18]. For the same reason, Li storage at turbostratic edges of hard carbon appears ideal for high power application due to a large amount of graphene layer edges arranged in a 'house of card' way that can potentially offer low activation energy to Li uptake/removal. So far, however, hard carbons were found to show a mixed Li-storage mechanism involving turbostratic edges, few layers graphene stacks and inner walls of the microporosity. Li-storage at turbostratic edges occurs at the highest potentials as a sloppy variation of the potential, whereas the two other mechanisms enable to store lithium ions at much lower and nearly constant potentials as proven by in-situ XRD or NMR studies [13], [19]. So in summary, hard carbon materials that show exclusive Li-storage at turbostratic edges have not yet been demonstrated. Carbon black (Super-P®, Csp) is one of the most common conducting additives in battery electrodes thanks to its low price, high electronic conductivity and low gravimetric surface. In the literature, very few reports are available for Li storage performance of Csp [20], [21]. Furthermore, neither the fundamental examination of the structure of Csp nor the mechanism of Li storage has been investigated to our knowledge. In this paper, we demonstrate via $operando$ XRD, ex-situ ^{7}Li-NMR, and HRTEM, that Csp enables Li storage to occur exclusively at turbostratic edges (Scheme 1) which brings excellent power capability and cycle stability. These specific advantages of Csp are further demonstrated through its use as the negative electrode of an LIC (Scheme 1).

2. Experimental section

2.1. Materials

Carbon super P® (Csp) conductive carbon black was purchased from TIMCAL, YP-80 from Kuraray chemical co. And activated porous carbon (AC) from ACS chemicals. Carbon nanotubes (CNT) were provided by Showa Denko (VGCF-X), graphite (MCMB) was purchased from MTI corporation and onion-like carbon (OLC) was synthesized by CIRIMAT laboratory, Université Paul Sabatier, Toulouse, France. 1 M $LiPF_6$ in EC:DMC (1:1 v/v) or LP-30 electrolyte were purchased from BASF and N-methylpyrolidone (NMP) was purchased from Aldrich.

2.2. Electrode preparation

Csp was mixed with 10 wt% PVDF in NMP and ball milled for 30 min at 600 rpm. The ink was roll coated on a Cu foil having a 20 μm thickness and mass loading was between 1 and 2 mg/cm^2. The positive electrode is typically made out of a mixture of activated carbon (4 mg/cm^2) containing 5 wt% Teflon and pressed on a stainless steel mesh at 5 Tons/cm^2.

2.3. Electrochemical characterization

Modified Swagelok cells with an inner diameter of 12 mm were used for electrochemical measurements. Electrodes were cut into the specific dimension and kept between glass fiber separators soaked in LP-30 electrolyte. Cell assembly was carried out in a moister free glove box (H_2O < 1 ppm, O_2 < 0.3 ppm). All electrochemical measurements were monitored by Bio-Logic VMP-2 or -3. Unless specified, the reference and counter electrodes are Li metal. For the full cell, activated porous carbon (AC) was used in the voltage window of 4.3 to 2.4 V for initial cycling and long-term cycling was carried out in the 4.3–2 V range. Pre-lithiation of Csp was carried out using a sacrificial Li metal electrode and followed by conventional charge-discharge against AC positive electrode. Considering the capacity of Csp and AC, a 1.0:2.6 mass ratio was used between the negative and the positive electrodes. AC/AC supercapacitors were assembled using two identical AC electrodes loaded at 4 mg/cm^2 and operated in a 0–2.7 V voltage window. Power characteristic was studied with varied current density from 0.1 mA/cm^2 to 5 mA/cm^2. Energy density and power density was calculated using Ec-Lab software using an equation E = $V*I*t$ (I is the current, V is the mid-voltage ≈ 3.35 V and t is discharge time) and P = E/t, respectively. Electrochemical impedance spectroscopy (EIS) was performed from 100 kHz to 0.01 Hz with a sinusoidal amplitude of 10 mV (Vrms = 7.07 mV). Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere using a Perkin Elmer apparatus. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) were performed using with Jeol JSM-7600F and Hitachi HF2000 microscopes (100 kV, Cold FEG), respectively. For TEM analysis, lithiated samples were prepared inside a glove box under argon atmosphere after washing and further transferred into the TEM using a vacuum transfer sample holder. Infrared spectra were directly collected from electrodes in ATR mode inside the glove box with the Alpha FT-IR spectrometer from Bruker.

2.4. MAS NMR

The electrodes were recovered after electrochemical cycling, washed with DMC, dried under vacuum at 40 °C for 6 h and packed in a 2.5 mm diameter zirconia rotor. MAS-NMR measurements were acquired on a Bruker Advance 200 spectrometer (B = 4.7 T) using the Larmor frequency of [7]Li 77.78 MHz. In order to remove the distorted baseline, a Hahn-echo pulse ^{7}Li NMR was performed at a spinning rate of 25 kHz with a non-selective pulse length of 1.4 μs and a recycle time of 5s.

2.5. Operando XRD

For $operando$ XRD, Csp powder was prepared as a film, pressed onto the surface of a beryllium current collector inside a homemade cell and separated by Li counter/ref by glass fiber separator. The Csp electrode was scanned continuously between 2θ values of 8 to 35° during the charge and discharge (C/10), one scan lasting for 12 min.

3. Result and discussion

Commercial Csp powder exhibits a specific surface area (SSA) of 63 m^2/g. Particles are nearly spherical in shape (40-45 nm diameter) as