



Short communication

## Wide-voltage-window silicon nanowire electrodes for micro-supercapacitors *via* electrochemical surface oxidation in ionic liquid electrolyte



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### ABSTRACT

The potential of silicon nanowires (SiNWs) as electrode material for large-voltage window micro-supercapacitors has been investigated. An ionic liquid electrolyte (EMI-TFSI) has been used in order to prevent the previously reported etching of silicon electrodes. Electrochemical oxidation of silicon surface at high anodic potentials leads to an extended operating voltage range (up to 4 V) and slightly enhanced specific capacitance of silicon electrodes. The ability of SiNW electrodes to operate at high frequency was demonstrated and a promising specific power of 472  $\mu\text{W cm}^{-2}$  was obtained.

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### 1. Introduction

The development of portable electronic devices, remote sensors and actuators require miniaturized, reliable and efficient integrated power sources. Micro-electrochemical capacitors are attractive candidates for energy storage due to their high power density, cycle life and charge/discharge efficiency [1,2]. In particular, carbon-based electrical double layer capacitors (EDLC) as well as metal oxide-based pseudocapacitors have attracted much attention over the last few years [3–6]. However, scaling down and on-chip integration remain challenging.

In this perspective, silicon nanowires (SiNWs) [7–9], silicon-based [10] and silicon carbide nanowires [11,12] have recently emerged as potential EDLC electrode materials enabling micro-scale integration though performances still need improvement to reach those of the most efficient carbon-based micro-supercapacitors such as carbide derived carbon or graphene/carbon nanotubes [2]. Promising areal capacitance and maximum power density have been demonstrated, with values up to 1.7  $\text{mF cm}^{-2}$  and 1.6  $\text{mW cm}^{-2}$ , respectively. Nevertheless, one of the main drawbacks of these systems arises from the relatively small voltage window, which usually does not exceed 1 V for silicon electrodes operating either in aqueous or organic electrolytes

[8–11,13]. A slightly wider electrochemical window of 1.3 V was also reported for porous silicon in ionic liquid electrolyte, and was further increased to 2.7 V after surface passivation with a graphene layer but at the cost of a supplementary CVD step at high temperature [14]. As the energy density of an EDLC is proportional to the capacitance of the electrodes and the square of the maximum voltage, further improvement of the SiNW supercapacitor performances largely relies on the ability to increase the voltage window [15]. Although the main limitation was attributed to silicon oxidation to  $\text{SiO}_2$  [8,10], the effect of silicon oxide coating on electrode properties has not been studied yet, due to the fact that silicon etching was concomitant to its oxidation [8].

In this work, we demonstrate that surface oxidation of silicon is a key parameter and can be performed electrochemically in a controlled manner provided that etching phenomena be avoided. Thus, the use of an ionic liquid as an electrolyte results in a strong enhancement of the operating voltage window of SiNW electrodes up to 4 V alongside an improvement of the specific capacitance.

### 2. Experimentals

#### 2.1. Preparation of silicon electrodes

Highly n-doped Si (111) substrates (doping level  $5.10^{18}$  As doping atoms  $\text{cm}^{-3}$ ) are prepared by (a) successive dipping and ultrasonication in acetone, then isopropanol, and (b) successive dipping in caro ( $\text{H}_2\text{SO}_4$ /

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H<sub>2</sub>O<sub>2</sub> 3:1), 10% HF and NH<sub>4</sub>F solution. For SiNW growth, 50 nm gold colloids are deposited on the surface from an aqueous gold colloid solution (BBI) with 10% HF. Highly doped n-type SiNWs with ca. 20 μm length, 50 nm diameter and 3.10<sup>8</sup> NWs cm<sup>-2</sup> density are grown via chemical vapor deposition as previously described [9,16,17].

## 2.2. Electrochemical characterization

All experiments were performed in a glovebox at room temperature in the dark in a three-electrode cell using an AutolabPGSTAT302 potentiostat/galvanostat equipped with a FRA 2 module. The electrolyte was 1 M NEt<sub>4</sub>BF<sub>4</sub> in propylene carbonate (PC) or 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI) ionic liquid. The nanostructured silicon nanowires (SiNWs) or bulk silicon substrates were used as working electrode (active area 0.39 cm<sup>2</sup>), the back side being in contact with a copper current collector. Pt wire was used as counter electrode and Ag/Ag<sup>+</sup> electrode was used as reference electrode (10<sup>-3</sup> M AgNO<sub>3</sub>, 1 M NEt<sub>4</sub>BF<sub>4</sub> in PC for use in organic electrolyte or 10<sup>-2</sup> M silver trifluoromethanesulfonate (AgTf) in EMI-TFSI for use in ionic liquid electrolyte). Electrochemical impedance spectroscopy (EIS) measurements were recorded by applying a 10 mV AC amplitude (frequency range 10 mHz–100 kHz).

## 3. Results and discussion

Electrochemical studies were performed on highly n-doped bulk silicon and SiNW electrodes. The cyclic voltammetry (CV) response observed for the bulk silicon in the 1 M NEt<sub>4</sub>BF<sub>4</sub> propylene carbonate organic electrolyte indicates that an electrochemical reaction takes place during the positive potential sweep (Fig. 1a). This can be ascribed to silicon oxidation and concomitant etching, as previously reported for SiNWs [8]. Silicon oxidation was attributed to the presence of water traces [18]. Etching is then expected to occur as the tetrafluoroborate anions BF<sub>4</sub><sup>-</sup> provide free fluoride F<sup>-</sup> for complexation of the oxidized silicon in nonaqueous organic electrolyte [19].

In order to impede silicon etching, the organic electrolyte was replaced with the fluoroborate-free ionic liquid EMI-TFSI. The first voltammogram shows several irreversible peaks (Fig. 1b) with a shoulder at 0.25 V and a main peak at 1.05 V vs Ag<sup>+</sup>/Ag that can be attributed to the oxidation of the topmost and underlying silicon atom layers, respectively [20]. These peaks disappear upon repeated cycling, indicating complete oxidation of the topmost and at least first underlying atom layer. A similar trend is observed for the SiNWs although the peaks are less defined and oxidation occurs at a slower rate, requiring more cycles (Fig. 1c). No sign of etching was detected in EMI-TFSI, demonstrating that it is a suitable electrolyte for electrochemical oxidation of silicon electrodes.

Oxidation of the silicon electrodes was controlled by applying repeated CV cycling treatment with increasing maximum anodic potentials. Electrochemical impedance spectroscopy (EIS) was used to study the capacitive behavior. Fig. 2 shows the evolution of the capacitance with the frequency as determined by EIS according to

$$C'(\omega) = \frac{-Z''(\omega)}{2\pi f |Z(\omega)|^2} \quad (1)$$

where  $C'$  is the real part of the capacitance,  $Z$  is the impedance,  $Z''$  is the imaginary part of the impedance and  $f$  is the frequency [21]. As evidenced on Fig. 2a, the capacitance of the bulk Si electrode increases slightly after oxidation of the topmost layer (CV up to 0.4 V vs Ag<sup>+</sup>/Ag) and reaches a two-fold increase after oxidation up to 1.2 V vs Ag<sup>+</sup>/Ag, i.e. after the second oxidation peak. A further increase in the maximum potential limit does not result in significant variations. SiNWs exhibit capacitance values ca. 10 times higher than capacitance

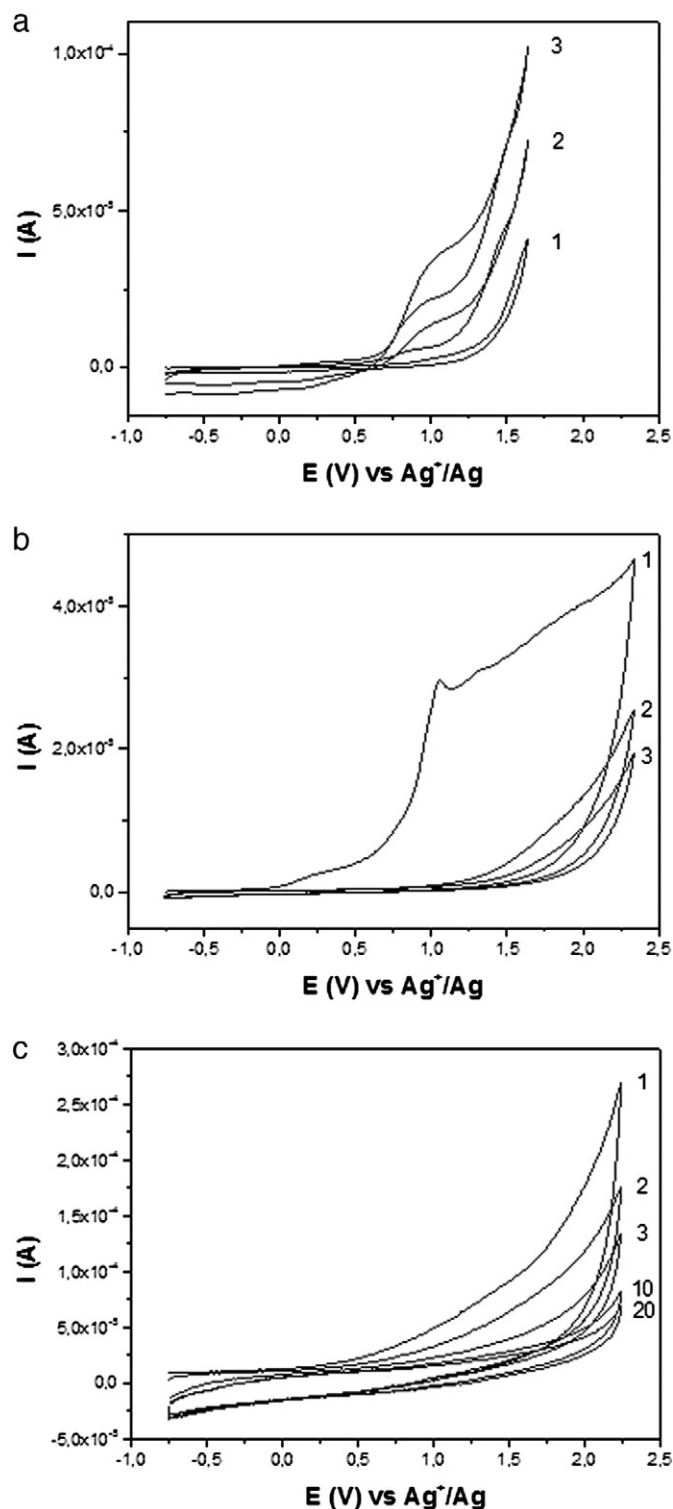


Fig. 1. CV of (a) bulk Si at 100 mV s<sup>-1</sup> in PC containing 1 M NEt<sub>4</sub>BF<sub>4</sub>, (b) bulk Si at 100 mV s<sup>-1</sup> in EMI-TFSI, and (c) 20 μm-SiNW electrode at 500 mV s<sup>-1</sup> in EMI-TFSI.

of bulk electrodes (Fig. 2b). The oxidation effect is less pronounced and deviation from the ideal behavior is observed below 1 Hz. However, the maximum capacitance is obtained after cycling up to 1.6 V vs Ag<sup>+</sup>/Ag, confirming the beneficial effect of surface oxidation of silicon. Going to higher potential results in reduced capacitance. In such case, the formation of a film is also observed on the electrode (Fig. 3a), possibly due to polymerization of intermediates generated upon electro-oxidation/degradation of imidazolium cations [22]. This deposition was not observed when keeping the maximum positive potential at

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