Understanding the energy storage mechanisms of poly(3,4-ethylenedioxythiophene)-coated silicon nanowires by electrochemical quartz crystal microbalance

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Abstract

The capacitive properties of electrodes elaborated from the electrochemical deposition of poly(3,4-ethylenedioxythiophene) (PEDOT) coatings onto chemical vapor deposition (CVD)-grown silicon nanowires (SiNWs) were investigated for supercapacitor applications. A high areal capacitance value of 17 mF cm^{-2} (50 F g^{-1}) was obtained at a scan rate of 100 mV s^{-1} in a 3-electrode cell configuration. Furthermore, this 3D hybrid nanostructure was analyzed by electrochemical quartz crystal microbalance (EQCM) to correlate the interfacial ionic exchange mechanisms to their electrochemical performance. It was demonstrated that both anions (BF$_4^-$) and cations (TBA$^+$) were simultaneously involved in the charge compensation during the oxidation-reduction scans of cyclic voltammetry measurements.

1. Introduction

During the last decade, doped SiNWs have awakened an enormous interest as promising electrodes in the field of (micro)-supercapacitors (SCs) due to their intrinsic properties in terms of quasi-ideal capacitive behaviour (rectangular shape cyclic voltammograms), wide operating cell voltage (up to 4V), large working temperature range (-40 to 60°C), good technical compatibility with the microelectronics industry (e.g. solder reflow process), high maximal power density (225 mW cm^{-2}), excellent coulombic efficiency (~99%) as well as an extraordinary cycling stability (up to millions of galvanostatic charge-discharge cycles) [1]. Despite of such outstanding electrochemical performances the comprehension of energy storage mechanisms concerning SiNW-based SCs has not yet been explored, which might play a crucial role in unveiling the chemical/physical processes involved during the charge-discharge cycles and thus, in the design of high performance next generation SCs. Within this context, *in-situ* and advanced simulation methods based on cutting-edge spectroscopy, scattering, imaging and electrochemical techniques have recently attracted a great deal of attention [2-4]. Among them, the electrochemical quartz crystal microbalance (EQCM) is a powerful tool to investigate the ionic exchange at the electrode-electrolyte interface, providing useful information about the capacitive properties of the electrode by analyzing the capacitive current and the resulting mass changes [5]. To date, in the area of SCs, EQCM has been widely employed in a great variety of carbon (nano)-structures (e.g. carbon nanotubes, activated carbon, carbide-derived carbon, or micro-porous carbon electrodes) or pseudocapacitive material films (e.g. MnO$_2$) [6]. More recently, we have reported a pioneer study concerning the potential of EQCM in the understanding of the supercapacitive behaviour of vertically-oriented graphene nanosheet (VOGN) electrodes, which had not been reported before in the literature [7]. Following these previous developments, in this study, a new approach dealing with PEDOT-coated SiNW electrodes will be investigated, for the first time, by EQCM revealing its excellent electrochemical performance as pseudocapacitor electrode [1].

2. Experimental

Growth of SiNWs. Highly n-doped SiNWs were grown in a CVD reactor (EasyTube3000 First Nano, a Division of CVD Equipment Corporation) via gold catalysis using an optimal vapor-liquid-solid deposition procedure [8]. Briefly, SiNWs were grown from a 12 nm evaporated thin gold film on GaPO$_4$ substrates (specific temperature resistant resonators for the EQCM experiments) using a reaction temperature of 600°C, under 6 Torr total pressure, with

40 sccm (standard cubic centimeters) of SiH_4, 100 sccm of PH_3 gas (0.2% PH_3 in H_2) for n doping, 100 sccm of HCl gas and 700 sccm of H_2 as supporting gas.

Electropolymerization of EDOT on SiNWs. PEDOT films were electrochemically deposited from a propylene carbonate solution containing 10 mM EDOT as the monomer and 0.1M tetrabutylammonium tetrafluoroborate (TBA BF$_4$) as electrolyte. The electropolymerization was conducted in a home-made 3-electrode cell configuration using a multichannel VMP3 potentiostat/galvanostat with Ec-Lab software (BioLogic, France). SiNWs was employed as the working electrode, a Pt grid as counter electrode and a non-aqueous Ag/Ag^+ reference electrode. The electrochemical deposition of PEDOT was carried out by chronoamperometry using a constant potential of 0.9 V (vs Ag/Ag^+) during 1h. All chemicals were purchased from Sigma Aldrich.

Electrogravimetric characterization with EQCM and evaluation of capacitive properties. A lab-made QCM device based on a Miller oscillatory circuit was used to measure the resonant frequency change Δf of the GaPO4 crystal (around 6 MHz), which is then converted into mass changes Δm using the Sauerbrey equation: $\Delta f = -k_s \cdot \frac{\Delta m}{A}$ where A is the electrode surface (0.2 cm^2) and k_s is the sensitivity factor (Theoretical value: $7.92 \cdot 10^7\ Hz\ g^{-1}\ cm^2$) [7]. A solution of acetonitrile containing 0.5 M TBABF$_4$ was used as electrolyte for the measurements, with a platinum grid as counter electrode and an acetonitrile-based Ag/Ag^+ reference electrode. This EQCM setup was employed to perform cyclic voltammetry (CV) combined with simultaneous mass variation measurements in a potential window from -1.5 V to 1V vs Ag/Ag^+ at a scan rate of 100 mV s^{-1}. More quantitative information from the EQCM data is obtained with further analysis, i.e. by means of the mass per mole of electron (MPE) estimation. This analysis provides the mass/charge ratio values as a function of applied potential during a CV scan, indicating the apparent mass of the ions involved in the charge compensation. Thus, MPE can be expressed according to the following equation [9,10]:

$$MPE = F\frac{\Delta m}{\Delta q} = F\frac{\Delta m/\Delta t}{\Delta q/\Delta t}$$

where F is the Faraday constant and Δq are the charge variations.

Areal capacitance (*AC*) was calculated according to the following formula, *AC=Q/(ΔVA)*, where *Q* is the average voltammetric charge, which is determined by integrating either the oxidative and reduction scans of the corresponding CV curve and *ΔV* is the potential range.

3. Results and discussion

Figure 1a and 1b show the morphology of SiNWs grown by CVD and electrochemically PEDOT-coated SiNWs deposited on GaPO$_4$ substrates. As can be seen in Figure 1a, a high density of SiNWs (~10^9 NW cm^{-2}) was deposited on the substrate, leading to a total mass of 220 µg cm^{-2} (determined by the QCM measurements before and after the deposition). The morphological characteristics of SiNWs were analyzed based on the SEM images (Figure 1) and revealed NW length of 10 µm and diameters ranging from 50 to 500 nm. Regarding its surface functionalization by electroactive conducting polymers, a nanometric PEDOT coating (thickness of ~100 nm) with a globular morphology was deposited along all nanowires, which was found to be similar to our previous work dealing with the electropolymerization of PEDOT in presence of ionic liquid electrolytes (e.g. PYR$_{13}$TFSI) [11]. Thus, according to Figure 1b, a uniform, adherent and conformal polymer coating, corresponding to a deposited PEDOT mass of 125 µg cm^{-2}, was achieved. The potential of these nanostructures, as capacitive electrodes, was evaluated by CV curves at a scan rate of 100 mV s^{-1} as displayed in Figure 2. Important differences concerning the working principle between both nanostructures was evidenced. Thus, SiNW electrodes exhibited an excellent electrochemical double layer capacitive behaviour associated to the electroadsorption and de-electroadsorption of ions during the charge-discharge processes (Figure 2a), whereas PEDOT-coated SiNWs reflected a characteristic electrochemical response associated to oxidation-reduction reactions of PEDOT (Faradaic reactions). Thereby, a clear peak at - 0.25V (oxidation) vs Ag/Ag$^+$ was recorded at a scan rate of 100 mVs^{-1} (Figure 2b), leading to an AC value of 13 mF cm^{-2}. This value was clearly found to be higher than that of bare SiNWs (AC: 38 µF cm^{-2}, Figure 2a), which was expected according to the pseudocapacitive nature of PEDOT.

Concerning the electrogravimetric response, EQCM data could not be obtained in the particular case of bare SiNWs because of the low mass variations. The noise observed in Figure 2a was ascribed to the hydrodynamic contribution and the viscoelastic properties of SiNWs. However, the SiNWs' electrogravimetric response was modified when covered with PEDOT and consequently significant mass variations of around 2 µg were measured upon cycling with points of zero mass change at 0.1V (oxidation) and -0.25V (reduction), indicating a major anion contribution above 0.1V and cation contribution below -0.25V (Figure 2b), respectively. Above

0.1V the value of the MPE is around 90 g mol^{-1}, which was found to be in good agreement with the molar mass of BF_4^- anions (86.8 g mol^{-1}). During a positive scan, these measurements indicate that TBA^+ cations are expelled from the PEDOT coating during the oxidation peak at -0.25V and over 0.1V, a capacitive process appears, which corresponds to the electro-adsorption of BF_4^- anions indicated by MPE values.

4. Conclusions

In this work, for the first time, we have unveiled the mechanisms of energy storage in PEDOT@SiNW-based supercapacitive electrodes by EQCM. The obtained results confirmed the important role of anions (BF_4^-) and cations (TBA^+) in the electrochemical performances during the charge-discharge processes. Consequently, EQCM has been demonstrated to be an excellent technique to bring valuable insights into the ionic exchange mechanisms in vertically oriented nanostructured capacitive electrodes for battery and supercapacitor applications. In this direction, further experimental studies will be necessary to adapt and overcome the technical challenges of EQCM for bare SiNWs.

Acknowledgements

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Figure Captions

Figure 1. SEM images of a) SiNWs grown on a GaPO$_4$/Ti (10 nm)/Pt (400 nm)/Au (12nm) substrate and b) PEDOT-coated SiNWs. c) Schematic illustration of a GaPO$_4$ substrate. Micrographs were recorded by using a Zeiss Ultra 55 microscopy at an accelerating voltage of 4 kV with a tilt angle of 45°.
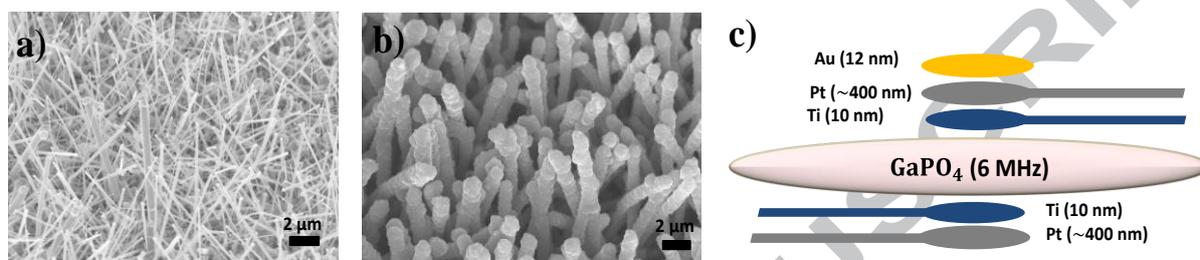
Figure 2. CV coupled with the mass measurement of a) SiNWs and b) PEDOT-coated SiNWs at a scan rate of 100 mV s^{-1}.
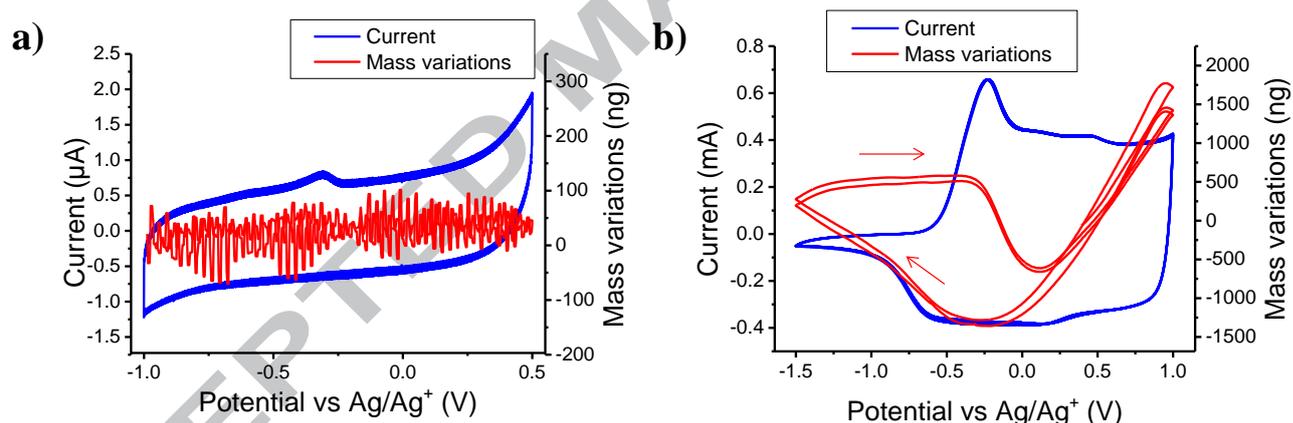
Highlights

- Electrochemically functionalized silicon nanowires by conformal polymer coatings.

- Specific capacitance of 50 F g^{-1} at a scan rate of 100 mV s^{-1}.

- Comprehension of mechanisms by electrochemical quartz crystal microbalance.

- Anions and cations play a key role on the electrochemical performance.