Uniform Coating of Polyaniline on Porous Carbon Nanofibers as Efficient Electrodes for Supercapacitors

Chau D Tran*, A.Q Vu, and Thang Van Le

Faculty of Materials Technology Ho Chi Minh City University of Technology, Vietnam National University Ho Chi Minh City Vietnam

Email: chau_tran@hcmut.edu.vn

Abstract. Porous activated carbon nanofibers (A-CNFs) are fabricated and considered as promising electrode materials for electrochemical double layer capacitors (EDLCs) due to their free-standing and hierarchical pore structure. They exhibit high specific capacitances in 1 M H₂SO₄ without any significant loss at high scan rates. To further enhance charge storage, we incorporated polyaniline onto A-CNFs with the aim to combine the benefits of both EDLCs (high power density) and pseudocapacitors (high energy density). By using a simple galvanostatic deposition, we achieve a uniform coating of polyaniline on A-CNFs. Combination of two different storage mechanisms results in an excellent specific capacitance of 290 F g⁻¹. Cyclic voltammetric measurements show no significant change at scan rates up to 100 mV s⁻¹.

1. Introduction

Supercapacitors are widely known as high-power energy storage devices that can be utilized for many practical applications. Depending on working mechanism, supercapacitors are divided into two types, namely electrical double layer capacitors (EDLCs) and pseudocapacitors. Carbon-based materials with a high surface area are typically used for EDLCs while fast faradic redox exhibiting materials, such as conducting polymer and metal oxides, are used for pseudocapacitors. Conducting polyaniline (PANI) has been shown as a promising material for pseudocapacitors due to its high theoretical pseudocapacitance (750 F g⁻¹) [1]. PANI exists in three different oxidation states: leucoemeraldine (fully reduced), emeraldine (half oxidized), and pernigraniline (fully oxidized). At low pH values, these states can get partially or fully protonated. Under electrochemically oxidizing condition, PANI transforms from leucoemeraldine to emeraldine, and finally to pernigraniline through the loss of electron. These reactions are also associated with a gain or loss of protons and anions. Depending on pKa value of electrolyte condition, transformation pathways of PANI will be different. Most of studies in the past have been carried out in an acidic solution, which is often linked with a high activity of polyaniline. Several reports [2-4] also tried to study in non-aqueous electrolytes to increase voltage window, but often associated with instability of PANI.

Polyaniline often faces a short cycle life due to the swelling and shrinking during the doping/dedoping process [5]. As an example, PANI expands due to anion insertion during transformation from leucoemeraldine to emeraldine. A thick PANI film will suffer an inefficient utilization at high power due to the long diffusion path length of ions. PANI with various nanostructures have been fabricated to reduce the diffusion path length; however, the reported sizes are still in the range...
of 50-300 nm [6]. Growth of nanostructured PANI on carbon based materials is often reported and provides an extremely high capacitance and a good cycle life. An example is the growth of PANI on porous carbon monolith [7]. The obtained specific capacitance with respect to PANI weight was 1580 F g\(^{-1}\), which is much higher than the theoretical value of PANI. However, the specific capacitance with respect to the total mass of PANI and carbon support was only about 300 F g\(^{-1}\). These composites are often impractical for commercialization due to either limited scalability or insignificant capacitive contribution from the carbon substrate [8]. Moreover, most works in the past synthesized powder-based electrodes. In this work, we demonstrate that conformal growth of nanostructured PANI on porous carbon nanofibers offers both high specific capacitance as well as stability upon cycling.

PANI can be deposited on carbon materials by either chemical or electrochemical method. Powder based electrodes are often obtained through the chemical method. As an example, previous studies have obtained a whisker-like or needle-like structure of PANI on graphitized carbon nanofibers (CNFs) [5, 9] by using oxidative polymerization. Before polymerization, nanofiber mats were ultrasonicated to obtain a uniform suspension of nanofibers. This resulted in loss of the free-standing morphology of nanofibers. Subsequently, the obtained PANI/CNFs powder needed to be mixed with a binder and conductive filler before coating on the current collector, resulting in reduced performance compared to free-standing materials. In contrast to chemical deposition, electrodeposition can be carried out on fabricated porous CNFs, while preserving their free-standing morphology. In this study, PANI will be coated on non-porous and porous activated CNFs which are both free-standing substrates using electrochemically galvanostatic technique. The non-porous carbon nanofibers (NP-CNFs) serve as a control substrate for initial studies on PANI electrodeposition. The porous carbon nanofibers (A-CNFs) are then utilized for PANI deposition to combine both aspects: double layer capacitance from porous carbon nanofibers and pseudocapacitance from polyaniline. We achieve a composite capacitance of 290 F g\(^{-1}\). The CVs show a near-rectangular shape with well-defined redox peaks up to 100 mV s\(^{-1}\).

2. Experimental

2.1 Fabrication of non-porous and activated porous carbon nanofibers

Polyacrylonitrile (Mw = 150000 g mol\(^{-1}\), purchased from Sigma-Aldrich) were dissolved in N,N-dimethylformamide (purchased from Sigma-Aldrich) at 10% w/w under gentle heating and stirring for 1h. Fibers were electrospun at room temperature under controlled humidity. The distance between the tip of the needle and the grounded collector was 5 inches, and the applied voltage of 12 kV was used to obtain a stable Taylor cone. The flow rate was kept at a constant of 1 mL h\(^{-1}\). The electrospun nanofibers were placed in a horizontal tube furnace and stabilized by heating to 280°C at a rate of 5°C min\(^{-1}\) under an air environment. The stabilized nanofibers were then carbonized by heating to 800°C at a rate of 5°C min\(^{-1}\) and held at 800°C for 1 hour under nitrogen atmosphere to obtain NP-CNFs. Then NP-CNFs was submerged in a 30% w/w KOH solution for 1h and activated at 800°C for 30 minutes to obtain A-CNFs.

2.2 Polyaniline deposition on non-porous and activated porous carbon nanofibers

Aniline (purchased from Alfa Aessars) was dissolved in 1M H\(_2\)SO\(_4\). The electrochemical polymerization of PANI on these substrates was carried out using a three-electrode cell containing Ag/AgCl as the reference electrode and a platinum mesh as the counter electrode. All reported potentials were versus Ag/AgCl. A T-type Swagelok cell was employed as shown in Figure 1. In this setup, a graphite rod of ½” diameter was used as the current collector. A ½” CNFs mat was placed between the graphite rod and a porous stopper and the assembly was compressed to minimize the contact resistance. The reference electrode was positioned such that it is sufficiently close to CNFs for lower solution resistance. The electropolymerization was carried out by holding a constant current density at 6 mA (galvanostatic). After deposition, samples were thoroughly washed with deionized water and dried at 60°C.
2.3 Electrochemical and structural characterization

The electrode materials are electrochemically tested by using cyclic voltammetry. The capacitance, $C$, is calculated by using the following equation:

$$C = \frac{1}{2} \frac{Q}{m \times V}$$

where $m$, $V$, and $u$ are mass of composite, voltage window and scan rate. The integral was done by using quick integrate feature of Echem Analyst software. The specific capacitance of polyaniline, $C_{\text{PANI}}$ (F g$^{-1}$PANI), was calculated by the following equation:

$$C_{\text{PANI}} = \frac{1}{2} \frac{Q - C_{\text{substrate}} \times m_{\text{substrate}} \times V}{m_{\text{PANI}} \times V}$$

where $C_{\text{substrate}}$ and $m_{\text{substrate}}$ are specific capacitance and mass of NP-CNFs or A-CNFs respectively, and $m_{\text{PANI}}$ is mass of PANI. The external morphology of electrospun nanofiber mats was characterized using scanning electron microscopy (SEM, Zeiss Supra 50VP). To characterize internal morphology, nanofibers were embedded in epoxy and microtomed into thin sections. The sections were then placed on lacy carbon copper grids and characterized using transmission electron microscope (TEM).

3. Results and discussion

The morphologies of free-standing carbon nanofibers were observed under SEM (Figure 2). Both NP-CNFs and A-CNFs show smooth surfaces with no visible porous structure. However, the TEM images of cross section of A-CNFs show clear intra-fiber pores. The appearance of porous structure inside A-CNFs was due to KOH which chemically etched carbon during heating at high temperature. The severely activating behaviour of KOH lead to a broad pore size distribution consisting of mesopores and micropores within nanofibers, which in turn resulted in high surface area carbon nanofibers.

![Figure 2. SEM images of the NP-CNFs (left) and A-CNFs (right) used for PANI deposition. The inset is the TEM micrograph of the microtomed section of A-CNFs.](image)

Free-standing carbon nanofibers were tested as electrode materials by cyclic voltammetry (CV) in a two-electrode cell. No binder or conductive filler was added to the free-standing films. As shown in Figure 3, the specific capacitance of A-CNFs was 120 F g$^{-1}$ while P-CNFs showed minor capacitance. CV curve of A-CNFs exhibited a near-ideal rectangular shape indicating an excellent rate handling
capability at 100 mV s\(^{-1}\). This was not only due to micro-textures of A-CNFS but also their inherent free-standing property which eliminated the usage of any insulating binder.

**Figure 3.** Cyclic voltammetry of NP-CNFS and A-CNFS at 100 mV s\(^{-1}\).

To further increasing the performance of these electrode materials, electropolymerization of PANI was carried out on these substrates. Electropolymerization of PANI depends on many factors: i) concentration of aniline, ii) concentration of electrolytes, iii) nature of the technique: potentiodynamic, potentiostatic or galvanostatic. In general, electropolymerization begins with aniline oxidation to form a radical cation which then reacts with a second radical cation to give a dimer while eliminating two protons [10]. The dimer or oligomer will then oxidize and react with another radical cation to build up the polymer chain.

Our initial investigation of electropolymerization using potential sweep technique between -0.1 and 1.0 V at scan rate of 20 mV s\(^{-1}\) in a solution containing 0.1 M aniline and 1 M H\(_2\)SO\(_4\) resulted in formation of degraded products instead of polyaniline. These degraded products were easily washed away with DI water indicating poor adhesion of the deposited materials. We increased aniline concentration to 0.5 M and reduced potential sweep between -0.1 and 0.9 V to minimize the formation of degraded products. Figure 4 shows SEM image of PANI deposition on NP-CNFS after 10 cycles of potential sweep. Non-uniform and non-conformal coating of PANI on outer surface of NP-CNFS can be easily seen. This result is similar to previous works on other carbon-based substrates [11-12]. The reason was probably due to the use of potentiodynamic technique which often associated with high current density and fast growth of polymer. These in turn affected the morphology of the deposited PANI.

**Figure 4.** SEM after depositing PANI on NP-CNFS using potential sweeping at 20 mV s\(^{-1}\) in 0.5 M aniline.

We switched to galvanostatic method by keeping the current density constant at 6 mA for 900 seconds for electropolymerization. Figure 5 shows a uniform and conformal coating of PANI on NP-CNFS. The SEM image of cross-section of PANI coated NP-CNFS revealed an approximated thickness of PANI around 100 nm. The deposited PANI on NP-CNFS was washed and then studied the electrochemical
behaviour in 1 M H$_2$SO$_4$. Figure 6 shows the CV curve of PANI on NP-CNfs. There is a high intensity of redox peak at 0.04 V and 0.2 V which corresponds to conversion between leucoemeraldine and emeraldine. The specific capacitance of PANI was approximately 500 F g$^{-1}$PANI with an assumption of negligible capacitive contribution of NP-CNfs. This value is comparable with several earlier reports [13-15]. However, the specific capacitance of the whole composite was reduced to 205 F g$^{-1}$ if we also counted the mass of NP-CNfs. This was understandable since NP-CNfs contributed a negligible amount of capacitance to the composite. In order to achieve higher capacitance of whole composite, we electropolymerized PANI on A-CNfs with the aim of integrating double layer capacitance of A-CNfs and pseudocapacitance of PANI.

![Figure 5. SEM after depositing PANI on NP-CNfs by keeping current density at 6 mA for 900 seconds.](image)

**Figure 5.** SEM after depositing PANI on NP-CNfs by keeping current density at 6 mA for 900 seconds.

![Figure 6. CV curve at 100 mV s$^{-1}$ after depositing PANI on NP-CNfs by keeping current density at 6 mA for 900 seconds.](image)

**Figure 6.** CV curve at 100 mV s$^{-1}$ after depositing PANI on NP-CNfs by keeping current density at 6 mA for 900 seconds.

Figure 7 shows the CV curve after depositing PANI on A-CNfs. The specific capacitance for the whole composite increased to 290 F g$^{-1}$PANI. At a similar loading of PANI, the PANI/A-CNfs composite capacitance is much higher than that of PANI/NP-CNfs sample. This is due to the higher capacitance contribution of A-CNfs (120 F g$^{-1}$) compared to NP-CNfs (negligible). This work demonstrated the fabrication of a true hybrid device integrating electric double layer and pseudo capacitance. Cheng et al. [16] deposited PANI on etched carbon fiber cloth by combining two different techniques: potentiostatic for initial nucleation and galvanostatic for a uniform deposition. They obtained a PANI nanowire coating, which showed a specific capacitance of 673 F g$^{-1}$. However, the specific capacitance of the whole composite was only 210 F g$^{-1}$ due to low capacitance contribution from the etched carbon fiber cloth. We achieved a composite capacitance of 290 F g$^{-1}$. Yang et al. [17] reported vein-like nanostructured PANI on activated CNfs using potentiodynamic approach. The CV curve is completely
distorted at a scan rate of only 10 mV s\(^{-1}\) indicating high resistance possibly due to larger PANI particle size. Their capacitance values decreased quickly with increasing scan rates to 70 mV s\(^{-1}\).

**Figure 7.** CV curve at 100 mV s\(^{-1}\) after depositing PANI on A-CNFs.

### 4. Conclusion

We studied the deposition of pseudocapacitive polyaniline on freestanding carbon nanofiber mats. By using galvanostatic electropolymerization method, we achieved a uniform and thin conformal coating of polyaniline on both NP-CNFs and A-CNFs. At the same loading of PANI, A-CNFs exhibited much higher capacitance than NP-CNFs due to the contribution from double layer capacitance of A-CNFs. The combination of two different storage mechanisms resulted in excellent specific capacitance of 290 F g\(^{-1}\) at 100 mV s\(^{-1}\). The thin conformal coating of PANI reduces the diffusion length of ions during doping/dedoping process of polyaniline for stability and high energy density at high power rate. This is evident from good capacitance retention even at a high scan rate of 100 mV s\(^{-1}\).

**References**

[1] G.A. Snook, P. Kao, A.S. Best 2011 *Journal of Power Sources* 196 1.

[2] F. Fusalba, P. Gouerec, D. Villers, D. Belanger 2001 *Journal of Electrochemical Society* 148 A1.

[3] J. Desilvestro, W. Scheifele, O. Haas 1992 *Journal of Electrochemical Society* 139 2727.

[4] W. Lu 2002 *Science* 297 983.

[5] J. Wei, J. Zhang, Y. Liu, G. Xu, Z. Chen, Q. Xu 2013 *RSC Advances* 3 3957.

[6] Y.G. Wang, H.Q. Li, Y.Y. Xia 2006 *Adv. Mater.* 18 2619.

[7] L.Z. Fan, Y.S. Hu, J. Maier, P. Adelhelm, B. Smarsly, M. Antonietti 2007 *Advanced Functional Materials* 17 3083.

[8] Y. Li, X. Zhao, P. Yu, Q. Zhang 2013 *Langmuir* 29 493.

[9] S. He, X. Hu, S. Chen, H. Hu, M. Hanif, H. Hou 2012 *Journal of Materials Chemistry* 22 5114.

[10] A. A. Syed, M.K. Dinesan 1991 *Talanta* 38 815.

[11] V. Gupta, N. Miura 2006 *Journal of Power Sources* 157 616.

[12] H.-F. Jiang, X.-X. Liu 2010 *Electrochimica Acta* 55 7175.

[13] D. Dhawale, A. Vinu, C. Lokhande 2011 *Electrochimica Acta* 56 9482.

[14] H. Khdary, M.E. Abdesalam, G. EL Enany 2014 *Journal of Electrochemical Society* 161 G63.

[15] H.-P. Cong, X.-C. Ren, P. Wang, S.-H. Yu 2013 *Energy and Environmental Science* 6 1185.

[16] D. He, C. Zeng, C. Xu, N. Cheng, H. Li, S. Mu, M. Pan 2011 *Langmuir* 27 5582.

[17] J.E. Yang, I. Jang, M. Kim, S.H. Baeck, S. Hwang, S.E. Shim 2013 *Electrochimica Acta* 111 136.