課題番号 :F-14-TT-0026
利用形態 :機器利用
利用課題名（日本語） :カーボンナノウォールの物性と応用
Program Title (English) :Properties and Applications of Carbon Nanowalls (CNW)

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1. 概要(Summary)

The possibility of enhancing the frequency performance of electrochemical capacitors by tailoring the nanostructure of the carbon electrode to increase electrolyte permeability is demonstrated. CNWs which are in direct electrical contact with the metallic current collector are produced via MPECVD growth on Ni and Cu. The resulting structure has a capacitance and frequency performance between that of an electrolytic capacitor and an electrochemical capacitor. The extension of capacitive behavior to the AC regime (~100 Hz) opens up an avenue for a number of new applications where physical volume of the capacitor may be significantly reduced.

Additional investigations on CNWs are listed in section 5. A manuscript is currently in preparation.

2. 実験(Experimental)

【利用した主な装置】

カーボン用プラズマ成膜装置

【実験方法】

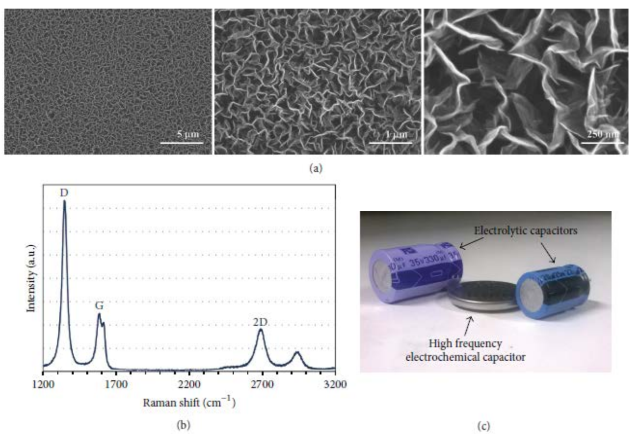

Figure 1: (a) SEM images of CNWs deposited onto Ni foil by MPECVD. (b) Typical Raman spectrum of CNWs on Ni substrate. (c) Size comparison of the CNW EC and electrolytic capacitors of similar capacitance.

Direct growth of vertically oriented CNWs onto various substrates by microwave plasma enhanced chemical vapor deposition (MPECVD) on metallic foils is used. Under our established standard conditions we obtain a uniform black, densely covered surface with vertically oriented graphene flakes forming a porous nanostructured 3D architecture (Figure 1). As a comparison, electrodes were also fabricated using state-of-the-art activated carbons. Electrochemical capacitors are fabricated by sandwiching 25 μm thick cellulose separators soaked in a solution of 1M tetraethyl ammonium tetrafluoroborate (TEABF4) in propylene carbonate and then packaged into type 2032 coin cells. Electrochemical properties of the capacitor were studied with an Autolab PGSTAT 302N.

3. 結果と考察(Results and Discussion)

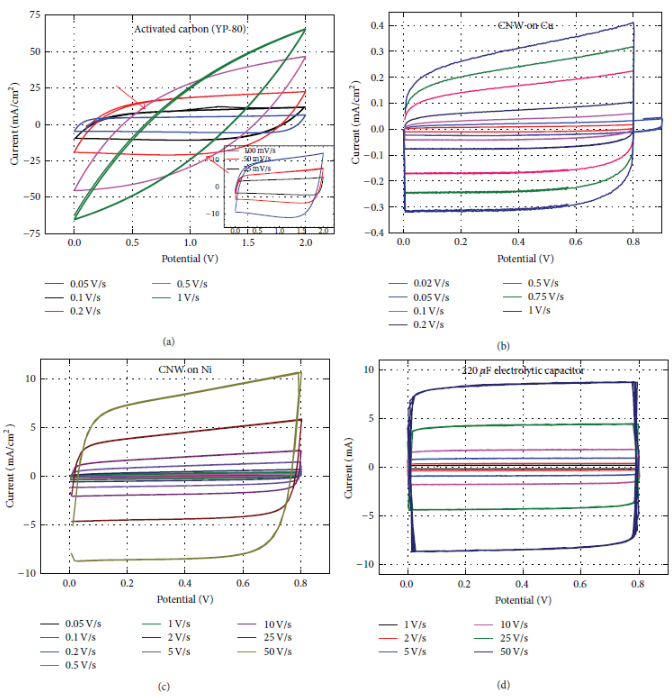

Figure 2: Cyclic voltammograms of (a) activated C electrodes,

(b) CNW on Cu electrodes, (c) CNW on Ni electrodes, and (d) a commercial 220 μF electrolytic capacitor.

Cyclic voltammograms of the four devices on study are shown on Figure 2. At slow scan rates, up to ~ 0.1V/s, the voltammogram of the activated carbon device (Figure 2(a)) has an almost rectangular (ideal) form but note that as scan rate goes up, the resistive component starts dominating and the curves tend towards a resistance-dominated behavior. Figures 2(b) and 2(c) show the voltammograms for CNWs on Cu and Ni, respectively. The rectangular shape is well maintained even at 50 V/s, already indicating better capacitive behavior at higher frequencies. Figure 2(d) shows measured voltammograms of a commercial electrolytic capacitor of similar capacitance, illustrating near-ideal behaviour.

Figure 3(a) shows the variation of current at midpoint of the cycle with scan rate for the different devices. A linear relation signifies constant capacitance with cycling rate which implies all the surface area of the electrode is easily accessible by the electrolyte at a fast rate, that is, high permeability. The electrolytic capacitor on the other hand maintains constant capacitance throughout the tested range. It should be noted that the absolute capacitance of the electrolytic capacitor is of similar magnitude to the CNW capacitor at higher frequencies, whilst still retaining a size advantage. However, it can be noticed from Figure 3(b) that at low scan rates the capacitance of the CNW capacitor goes up to ~3x the value at fast scan rates. Peak capacitances at (50mV/s) are 0.6, 205, and 0.18mF for the CNW, activated carbon, and electrolytic device, respectively. Figure 3(c) shows a Bode phase plot of the capacitors studied. All capacitors show capacitive behavior (near -90° phase angle) at low frequency and resistive behavior (near 0° phase angle) at high frequency. However, the transition occurs below 1Hz for the activated carbon device, whilst the CNW capacitors start changing above 100Hz. The electrolytic capacitor tested decayed at around 1000 Hz. Again, this disparity can be ascribed to electrode porosity differences.

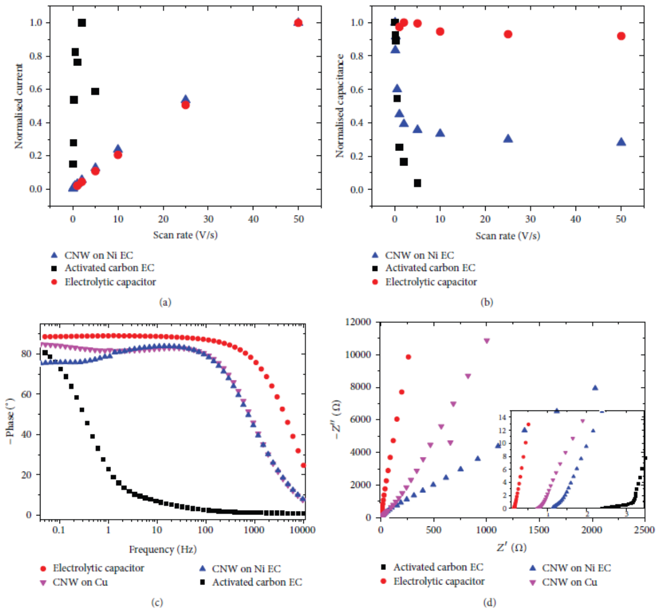

Figure 3: (a) Normalised current versus scan rate. (b) Normalised capacitance versus scan rate showing the rate of decay of capacitance with increasing scan rates. (c) Bode phase plot. (d) Electrochemical impedance spectroscopy data expressed as Nyquist plots over the frequency range of 10 kHz–0.05Hz. Inset shows zoom at low impedance.

4. その他・特記事項(Others)

None

5. 論文・学会発表(Publication/Presentation)

(1) P. Hiralal, Gemma. Rius, P. Andrew, M. Yoshimura, G. A. J. Amaratunga J. Nanomaterials 2014, 619238.

(2) Gemma Rius "Role of graphene as a modifier of metal surfaces for electrochemical cell charge storage" EMN Spring 2014, Las Vegas USA - Invited talk

(3) Gemma Rius, Jijeesh R. Nair, Matteo Destro, Pravin Jagadale, Masamichi Yoshimura, Alberto tagliaferro and Claudio Gerbaldi. "CNWs as potential high power anode for Li-ion microbatteries" ICPlasma Nagoya, Japan March 2015 – Poster presentation

(4) Gemma Rius "Nanostructuring and applications of carbon nanomaterials based on alternative approaches" Symposium on Next generation materials for challenges in energy and environment NITech August 2014 - Invited talk

６．関連特許（Patent）

None