Swiss roll nanomembranes with controlled proton diffusion as redox micro-supercapacitors†

Hengxing Ji,* Yongfeng Mei* and Oliver G. Schmidt

Received 16th February 2010, Accepted 21st April 2010
First published as an Advance Article on the web 7th May 2010
DOI: 10.1039/c003215h

We demonstrate a redox Swiss roll micro-supercapacitor by rolling up a multilayered nanomembrane with an electrochemical active layer at either the outer or inner surface for different proton diffusion behaviors. The Swiss roll micro-supercapacitor could achieve high performance (e.g. capacity and life time) in a microscale power source and is helpful for studying charge transfer at the electrolyte/electrode interface.

Nanotechnology has emerged as an exciting approach for energy applications, because it can not only effectively improve device performance but also generate microscale power supply units like silicon nanowire solar cells and heat–electricity conversion, and piezoelectric nano-generators. Very recently, coaxial nanostructures were suggested for high-performance lithium batteries due to improved electronic conductivity and Li storage. Furthermore, it was found that a three-dimensional nanoelectrode can enhance the battery capacity by 10 times over that of a 2D system. Rolling-up batteries is an industry-standard to manufacture commercial batteries on the macroscale. On the micro- and nanoscale, a roll-up technology has also been developed more recently for many potential applications, which show great opportunities towards individual coaxial Swiss roll micro- and nanostructures for energy storage applications.

In this study, we demonstrate a single Swiss roll redox micro-supercapacitor by rolling up a multilayered nanomembrane. The active material (RuO₂) for electrochemical energy storage is deterministically rolled-up at either the inner or outer surface of the fabricated tubular rolls, which causes different proton diffusion behavior at different working frequencies. Such Swiss roll microtubes may be applied to micro-scale energy storage devices with high performance, and are helpful to study charge transfer at the electrolyte/electrode interface.

The redox micro-supercapacitor was fabricated by rolled-up nanotechnology as depicted in Fig. 1(a). First, a multilayer nanomembrane consisting of a sacrificial and several functional layers was deposited on a Si/SiO₂ substrate. Second, the sacrificial layer was selectively removed by chemical etching. The etched area of the multilayer nanomembrane rolls up automatically into a tubular structure driven by strain release. We use photoresist as the sacrificial layer, and either an Au/RuO₂ or a RuO₂/Au/carbon nanomembrane as the functional layers to prepare Swiss roll microtubes with an electrochemical active layer (25 nm thick RuO₂), at either the outer or inner surface of the microtube (named as o-Tube and i-Tube, respectively, See Supplementary Information Fig. S1 for detailed parameters†). An optical image of the o-Tube is shown in Fig. 1(b), in which the tube is approximately 7 μm in diameter with around 7 windings deduced from the rolling length of 150 μm. The i-Tube has a comparable diameter. Fig. 1(c) presents an optical image combined with a sketch of our testing setup. The Swiss roll microtube was bonded to a conductive capillary, and then inserted by micromanipulation into an electrolyte solution to serve as the work electrode. The microelectrode is approximately 300 μm in length as viewed inside the electrolyte solution. This special set-up ensures that the charge/discharge current originates entirely from the Swiss roll microtube and simplifies the electrochemical characterisation. The electrochemical properties of a single Swiss roll microtube were first characterized by a cyclic voltammetry method. The results for the o-Tube are depicted in Fig. 2(a) at

† Electronic supplementary information (ESI) available: Experimental process, XPS and XRD measurements on RuO₂, and the dependence of voltammetric charge on the scan rate. See DOI: 10.1039/c003215h
various scan rates. The curves assume a rectangle-like shape and the current is proportional to the scan rate. This behavior can be observed at scan rates of up to 800 mV s\(^{-1}\). The curves of the i-Tube (not shown) look similar. The \(I-E\) curve of a \(\phi = 50 \mu m\) gold wire which has a circumference close to that of the rolling length of the microtube is presented for comparison. The response current of the gold wire is negligible compared to that of a microtube at the same scan rate. This result clearly reveals electrochemical reversibility of the Faradaic redox transition, which is typical for the redox capacitive behavior of amorphous RuO\(_2\).\(^{1c}\) The calculated capacitance is approximately 1.0 \(\mu F\) at a scan rate of 100 mV s\(^{-1}\) for a single Swiss roll microtube by integrating the anodic or cathodic charge.\(^{1c,d}\) The specific capacitance is calculated by dividing the redox capacitance by the rolling area. The value is approximately 2200 \(\mu F\) cm\(^{-2}\), which is close to that of the theoretical redox capacitance of anhydrous RuO\(_2\).\(^{1i,6}\) and larger than most previous experimental measurements from anhydrous RuO\(_2\) nanostructures.\(^7\) Remarkably, the feature size reduces from the millimetre size of a commercial 1 \(\mu F\) capacitor to the micrometre size of a Swiss roll redox micro-supercapacitor. The necessary 2D area for integrating a rolled-up supercapacitor on-chip is reduced to \(~1/20\) of that of the unrolled planar film. The stability and reversibility of the redox micro-supercapacitors were tested at different scan rates as depicted in Fig. 2(b). The capacitance holds the same level, even after a thousand cycles at different scan rates, implying excellent stability and reversibility of the devices.

The electrochemical properties of such a redox micro-supercapacitor were further studied by AC impedance spectroscopy. The complex-plane plot of the o-Tube, shown in Fig. 2(c), is composed of a nearly vertical line in the low frequency range of 40 mHz–320 Hz and a semicircle in the high frequency range of 0.5 MHz–5 MHz (Supplementary Information, Fig. S3\(^f\)). The vertical line represents an ideal capacitor behavior while the semicircle is caused by a parallel combination of resistance and capacitance.\(^{1c,8}\) The line below the knee frequency (around 320 Hz, in the inset of Fig. 2(c)) corresponds to the capacitor behavior and reaches higher frequencies than those of most electrochemical electrodes. For instance, knee frequencies of RuO\(_2\) nanorods and nanoparticles have been reported around 250 Hz and 2 Hz, respectively.\(^{7a,b}\) The Faradaic charge-transfer resistance, \(R_f\), can be deduced from the intersection of the semicircle in the high frequency range with the real axis.\(^{1c}\) The calculated \(R_f\) is around 0.1 \(\Omega\) cm\(^2\). This low value implies easy proton exchange between the electrolyte and the RuO\(_2\) layer in the rolled-up microtube. The low Faradaic charge-transfer resistance and high knee frequency may be attributed to the rolled-up multilayer nanomembrane structure: (1) The small thickness of the RuO\(_2\) layer (25 nm) reduces the proton diffusion length in the electrode, thus allowing for fast proton exchange between the electrode and electrolyte; (2) the gold layer enables efficient electron collection and conduction. This means that the design takes advantage both of the good manipulability of a one-dimensional microstructure and enhanced reaction kinetics of a thin film nanostructure, thus rendering the Swiss roll redox micro-supercapacitor highly stable and reversible.

Ion diffusion is a key issue in understanding and further enhancing the performance of electrochemical energy storage devices.\(^{1c,f}\) The Swiss roll microtube possesses a hollow core, a multilayer rolled-up wall, and the tube diameter and rotation can be readily controlled. Thus the proton diffusion behavior of the redox micro-supercapacitor can be tuned in order to analyze the effect of proton transport on the performance of a supercapacitor. According to the study of Trasatti et al.,\(^9a\) the stored total charge (\(Q_T\)) can be divided into two parts: \(Q_i\) contributing to the less accessible surface where diffusion is negligible compared to reaction rates. The different charges can be estimated from the dependence of charge, \(Q\), versus scan rate, \(v^{-1/2}\) (Supplementary Information, Fig. S4\(^f\)). The ratios of \(Q_i/Q_T\) calculated from the o- and i-Tube are 0.69 and 0.72, respectively, as shown in Table 1; and both are larger than that of a RuO\(_2\) nanocrystalline film, which lies between 0.1–0.3.\(^{9b,c}\) This result implies that the charge storage properties of the o- and i-Tube are similar when the scan rate is less than 800 mV s\(^{-1}\). However, the diffusion effect in the Swiss roll microtubes is enhanced compared to that in a nanocrystalline film.

The AC impedance spectra of the o-Tube, the i-Tube and a planar film of 25 nm RuO\(_2\) on a \(\phi = 50 \mu m\) gold wire are given as Bode plots in Fig. 3 for further analysis of the diffusion effect. The Bode plot of the o-Tube is composed of a small plateau at a frequency close to \(10^3\) Hz and a phase angle of around 45°, which indicates Warburg-like semi-infinite linear
diffusion behavior. In the lower frequency range, the phase angle approaches 90° which reflects an almost pure resistive-capacitive behavior. This effect is attributed to the fact that the outer surface of the o-Tube contacts the electrolyte directly, while the inner windings are in a confined space, which leads to a concentration polarization of reacting species. This concentration polarization has to be cancelled by reacting species (here: protons) diffusing from an accumulation side to a depletion side. In the case of the RuO₂ layer at the inner surface of the microtube (i-Tube), the whole reacting surface is in a confined space, and the Bode plot of the i-Tube reveals a wider plateau and is located at a lower frequency range compared to that of the o-Tube. This is due to an increase in proton diffusion which controls charging. However, both the o-Tube and the i-Tube present resistive-capacitive behavior at low frequencies owing to the fact that the charge/discharge time is long enough to cancel the proton diffusion effect. There is no feature of diffusion controlled reaction in the Bode plot of the unrolled planar film (blue curve in Fig. 3) since there is no confined space to control the proton diffusion. This result is consistent with the data in Table 1, which means the charge Q_r related to the diffusion controlled reaction contributes less to charge storage in the planar film compared to that in Swiss roll microtubes.

In conclusion, a three-dimensional Swiss roll redox micro-supercapacitor was demonstrated by rolling up a multifunctional nanomembrane. The proton diffusion behavior of the supercapacitor can be readily tuned by controlling the tube structure for analyzing the diffusion effect on the supercapacitor performance. This technique can be further applied to electrochemical microprobes in cell electrophysiology and local detection of microenvironments.

We thank Stefan Baunack, Steffen Oswald, Elliot J. Smith and Cornelia Krien for help. H.X.J. is grateful to the Alexander von Humboldt Foundation for fellowship support. This work was financially supported by Grants from the Volkswagen Foundation (I/84 072), a Multidisciplinary University Research Initiative (MURI) sponsored by the U. S. Air Force Office of Scientific Research (AFOSR) Grant No. FA9550-09-1-0550, and the German Research Foundation (DFG) within the International Research Training Group 1215.

Notes and references


