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Comparison of the electrochemical behaviour of buckypaper and polymer-intercalated buckypaper electrodes

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ABSTRACT

The performances of freestanding carbon nanotube (buckypaper) and polymer-intercalated buckypaper electrodes in an electroanalytical chemistry context were evaluated via analysis of direct current and Fourier Transform large-amplitude alternating current voltammograms derived from the ferrocenemonocarboxylic acid (FMCA$^{0/+}$), ruthenium hexamine ($[Ru(NH_3)_6]^{3+/2+}$) and ferricyanide ($[Fe(CN)_6]^{3-/4-}$) redox couples. The composite polymer-intercalated buckypaper electrodes exhibit substantially superior Faradaic-to-capacitive background charging current ratios under both dc and ac conditions compared and display close to ideal voltammetry for all three processes. A significant difference was detected in mid-point potentials determined by cyclic voltammetry at buckypaper and polymer-intercalated buckypaper electrodes, commensurate with different mass transport mechanisms. It is proposed that the porosity of the buckypaper gives rise to a restricted diffusion model of mass transport within the pores and a large electrode over that generates a large capacitance current. Thus, polymer intercalation is required to achieve high quality electroanalytical performance. Simulations of voltammograms obtained at porous polymer-intercalated buckypaper electrodes are consistent with the composite electrodes consisting of a randomly arranged array of nano-/micro-electrode domains, implying that significant surface heterogeneity is present. However, under slow scan rate conditions, when significant overlap of diffusion layers occurs, voltammograms may be approximately interpreted in terms of a linear diffusion based mass transport model.

1. Introduction

Applications involving carbon nanotubes (CNTs) are many and varied due to their interesting physical, chemical and mechanical properties [1–3]. One method to further enhance the usefulness of CNTs in materials and electrochemical applications has been to prepare them into free-standing films, often referred to as buckypaper [4]. However, compared to individual CNTs, the mechanical and structural properties of buckypaper are relatively poor. This is largely related to the weakly bound and randomly packed bundles of CNTs formed during processing, which results in the paper having between 60% and 70% of its volume as free space [5]. The majority of the free space is typically made up of interbundle pores or small macropores, whose sizes range from 10 to 1000 nm in diameter [5,6]. Intercalation of polymers into the buckypaper free space, either *in situ* or post-production, has proven to significantly improve its mechanical properties [5,7,8]. The use of naturally occurring biopolymers, such as DNA and chitosan, has been shown to produce buckypaper that is sufficiently conductive and mechanically strong, and suitable for use as biocompatible electrodes [9].

The electrochemistry at electrodes modified with CNTs has been intensively investigated during the last two decades [10]. The electrochemical reactivity of CNTs has been considered similar to that of highly-ordered pyrolytic graphite electrodes, composed of basal- and edge-plane sites possessing different reactivities, kinetics or electron transfer properties [11]. Imperfections are assumed to arise during the growth process or during sonication to disperse the CNTs or during the fabrication process for CNT electrodes. The CNTs may also contain impurities such as graphite particles, carbon nanoparticles, other forms of carbon, and residual metal based catalysts [5,12–14].

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To date, there have been few reports on the electrochemical characteristics of buckypaper electrodes [9,15]. In the present investigation, we compare bare buckypaper and buckypaper that has been intercalated with a series of non-conducting and conducting polymers. We report on their electrochemical properties as revealed by dc and large-amplitude ac voltammetric studies of three standard redox couples that encompass the three charged states of neutral, negative and positive, viz. the oxidation of ferrocenemonocarboxylic acid ($FMCA^{0/+}$), the reduction of ferricyanide ($[Fe(CN)_6]^{3-/4-}$), and the reduction of ruthenium hexamine ($[Ru(NH_3)_6]^{3+/2+}$).

2. Experimental section

2.1. Chemicals

Ferrocenemonocarboxylic acid (FMCA) (Sigma–Aldrich, 97% purity), KCl (AR BDH), $K_4[Fe(CN)_6]{\cdot}3H_2O$ (AR Ajax Finechem), $[Ru(NH_3)_6]Cl_3$ (Sigma–Aldrich, 98% purity), phosphate buffer saline (PBS) tablets (Sigma–Aldrich), single-walled carbon nanotubes (CNI nanotechnologies; lot P0317), Triton-X100 (AR. BDH), Ethanol (Univar, 95% purity), toluene (AR. Univar), poly(styrene-β-isobutylene-β-styrene) ($M_W = 160{,}362$, a gift from Boston Scientific), polystyrene ($M_w = 45{,}000$, Aldrich) and polyisobutylene ($M_w = 500{,}000$, Aldrich) all were used as received from the manufacturer. Poly(3-octyl pyrrole) (Fe-DBSA dopant) and poly((*E*)-4,4″-didecoxy-3′-styryl[2,2′:5′,2″]terthiophene) (an average polymer length of 11 monomer units, ~7.2 kDa) were chemically synthesized by the Intelligent Polymer Research Institute (Wollongong, Australia). Water derived from a Milli-Q purification system (resistivity 18 MΩ cm) was used to prepare aqueous solutions. A PVDF membrane (Durapore® Membrane Filters, Millipore) with a pore size of 0.22 μm was used for vacuum assisted filtration of the CNT dispersion solution.

2.2. Preparation of buckypapers and intercalation

The preparation of single-walled carbon nanotube (SWCNT) buckypaper and polymer-intercalated buckypaper are described in detail elsewhere [5,7]. SWCNT soot was used for fabrication of buckypaper without further purification. The dispersion solution of 120 mg SWCNT in 240 mL of 1% v/v Triton-X100 aqueous solution was prepared using horn sonication (pulse on for 1 s and off for 1 s) for 3 h, followed by bath sonication for 2 h. The solution obtained was filtered through a 0.22 μm pore size hydrophobic PVDF membrane linked to a vacuum line. The obtained buckypaper was washed several times with water until the bubbles of the surfactant disappeared, indicating that the majority of the surfactant had been removed. After washing with water, the buckypaper was then rinsed with ethanol and then allowed to dry. The functionalising or adsorbed surfactant is present in the buckypaper materials at a small level. The average thickness of resultant buckypaper lies in the range of 50–70 μm. The dried buckypaper was cut into rectangular strips (0.5 cm × 2.5 cm). The polymer was intercalated into the buckypaper architecture via soaking the buckypaper in a polymer solution for given periods of time. The solutions of poly(styrene-β-isobutylene-β-styrene), polystyrene and polyisobutylene were prepared at the concentration of 5% w/v in toluene while poly(3-octyl pyrrole) solution was of 0.125 % w/v in dichloromethane. Poly((*E*)-4,4″-didecoxy-3′-styryl[2,2′:5′,2″]terthiophene) solution was used at a concentration of 0.027 % w/v in toluene. Finally, the polymer-intercalated buckypaper strips were used as electrodes after carefully washing in toluene and drying at room temperature for 24 h. The sample weights before and after intercalation were measured using a microbalance (Sartorius) to determine the weight percentage of polymer intercalation. For convenience, the unmodified and poly(styrene-β-isobutylene-β-styrene), polystyrene, polyisobutylene, poly(3-octyl pyrrole) and poly((*E*)-4,4″-didecoxy-3′-styryl[2,2′:5′,2″]terthiophene) intercalated buckypaper electrodes will be referred to as BP, SIBS–BP, PS–BP, PIB–BP, POP–BP and PTP–BP, respectively.

2.3. Instrumentation and electrochemical procedures

The morphology of the BP architecture was investigated using a JEOL Scanning Electron Microscope. To obtain the cross-sectional images, the BP was frozen in liquid nitrogen and carefully snapped open to expose the interior.

All electrochemical experiments were performed with instrumentation capable of generating a sinusoidal ac waveform of frequency, f, and amplitude, ΔE, superimposed onto the triangular dc ramp which was swept over the potential range of interest at a given scan rate, v. Full details of the instrumentation are described elsewhere [16]. When large ac amplitudes are used, second and higher order harmonics are generated. These can be resolved by Fourier Transformation of data in the time domain to give the power spectrum (frequency domain) followed by band selection (filtering) and then Inverse Fourier Transformation to give the individual harmonics (time domain) as also described in Ref. [16]. For dc cyclic voltammetry, the amplitude of the applied sinusoidal waveform was set to zero. Experiments were carried out using a three-electrode cell containing a BP type working electrode, a Ag/AgCl (3 M NaCl) reference electrode and a platinum wire auxiliary electrode. Voltammetric studies at an edge-plane graphite (EPG) working electrode was also undertaken to provide comparative information. The BP electrode was connected to an alligator clip, suspended in the solution, with careful attention given to keeping the connection well above the solution level. The area of the EPG electrode was determined by comparisons of experimental data with that obtained by simulations using DigiSim software [17]. The diffusion coefficients, D, used in this and other simulations were: 7.6×10^{-6}, 6.3×10^{-6}, 7.6×10^{-6}, $7.8 \times 10^{-6}\ cm^2\ s^{-1}$ for $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$, respectively, and $6.0 \times 10^{-6}\ cm^2\ s^{-1}$ for both $FMCA^0$ and $FMCA^+$. All voltammetric experiments were undertaken at room temperature (293 ± 2 K) in pH 7.4 phosphate buffer solutions containing 0.1 M KCl as the supporting electrolyte. High-purity nitrogen was bubbled into the solution for at least 5 min to remove oxygen before commencing each experiment. The uncompensated resistance, R_u, for the cell was typically less than 100 Ω.

2.4. Simulations

Simulations of the dc cyclic voltammograms presented in this paper refers to solution-phase, one-electron charge transfer processes, in which species Red is oxidised to Ox (or species Ox is reduced to Red). Simulations were undertaken on the basis of the Butler–Volmer model for electron transfer and linear or other designated forms of diffusion. Thus, the oxidation process is summarised by following equation:

$$\mathrm{Red} \underset{k_b}{\overset{k_f}{\leftrightarrow}} \mathrm{Ox} + e^- \tag{1}$$

where k_f and k_b are the forward and backward electron transfer rate constants respectively.

In accordance with Butler–Volmer kinetics

$$k_f = k^{0'} \exp\left[\frac{\alpha nF}{RT}\left(E(t) - E^{0'}\right)\right] \tag{2}$$

$$k_b = k^{0'} \exp\left[\frac{-(1-\alpha)nF}{RT}\left(E(t) - E^{0'}\right)\right] \tag{3}$$