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Fast Electron Transfer Kinetics on Multiwalled Carbon Nanotube Microbundle Electrodes

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ABSTRACT

The rate of electron transfer at carbon electrodes depends on various factors such as the structure and morphology of the carbon material used in the electrodes. With the advent of new carbon structures, such as fullerenes and carbon nanotubes, well-defined carbon surfaces have become available to probe electron-transfer kinetics on these surfaces. We show here that micron-size electrodes made of multiwalled carbon nanotubes show Nernstien behavior and fast electron-transfer kinetics for electrochemical reactions of $Fe(CN)_6^{3-/4-}$. This is achieved without any pretreatments for the electrodes, suggesting the possibility of developing superior carbon electrodes based on carbon nanotubes, for electrochemical applications.

Since the days of Michael Faraday, different carbon structures have been studied as electrode material.[1] Presently, electrodes made from various carbon materials (partially graphitized glassy carbon, activated carbon, and graphite fibers) are widely used in important electrochemical applications,[1−3] for example, fuel cells.[4] Several works have focused on understanding the factors that govern electron-transfer kinetics on carbon electrodes. The surface structure of the solid carbon electrodes directing electron transfer (ET) reactions in electrochemistry has been well recognized, and it is found that the creation of specific surface structures, through pretreatments such as plasma activation,[5] can drive the ET faster. The surface preparation and, hence, the final surface structure is often found to be critical to the performance of the electrodes, its stability and reproducibility of results. The surface modification effects are also sensitive to the reaction that is being conducted at the electrodes.[6] Thus, different reactions should be considered when addressing the role of the electrode surface on the ET mechanism.

The oxidation of potassium ferrocyanide has served as a benchmark in investigating electrochemistry at different carbon electrodes.[2] The electrochemical oxidation generates ferricyanide, and the redox couple $Fe(CN)_6^{4-}$ /$Fe(CN)_6^{3-}$ is close to an ideal system with quasi-reversibility, especially on electrodes (such as carbon) where there is minimum bonding interaction between the electrode material and the cations in solution. When using metal electrodes such as Pt, the kinetics of the reaction could be affected by the nature of the cations in the medium.[7] When the metal electrode dimensions are small (e.g., use of Pt nanoelectrode reported[8] recently), care must be taken to delineate problems associated with adsorption of redox species ($Fe(CN)_6^{4-}$) and so forth and to make sure that the data obtained is reproducible over extended periods of time. However, the importance of this redox couple in electrochemistry also stems from its role in instrument calibration, determination of diffusion coefficients and the electrochemical area of the electrode. This reaction on most electrodes precludes any effect of surface adsorption (oxide layer formation) on the ET kinetics and hence provides a straightforward correlation of the surface structure and reaction rates. For this reaction, at the basal planes of highly ordered pyrolytic graphite (HOPG) the cyclic voltammetric curve is quasi-reversible with peak potential separation (ΔE_p) $>$700 mV, indicating very slow ET rate. On graphite edge planes, ET occurs much faster with a ΔE_p value of ∼70 mV (at the same sweep rates). With electrochemical pretreatments (such as application of a potential to the carbon electrodes in solution, e.g., KNO_3), the ΔE_p value for basal planes can be brought up to ∼100 mV[2]. Similarly, the pretreatment of glassy carbon by laser activation produces near ideal surfaces for ET kinetics producing, ΔE_p of ∼60 mV. All these experiments show that the surface of graphitic carbon plays a significant role in determining the ET kinetics and in

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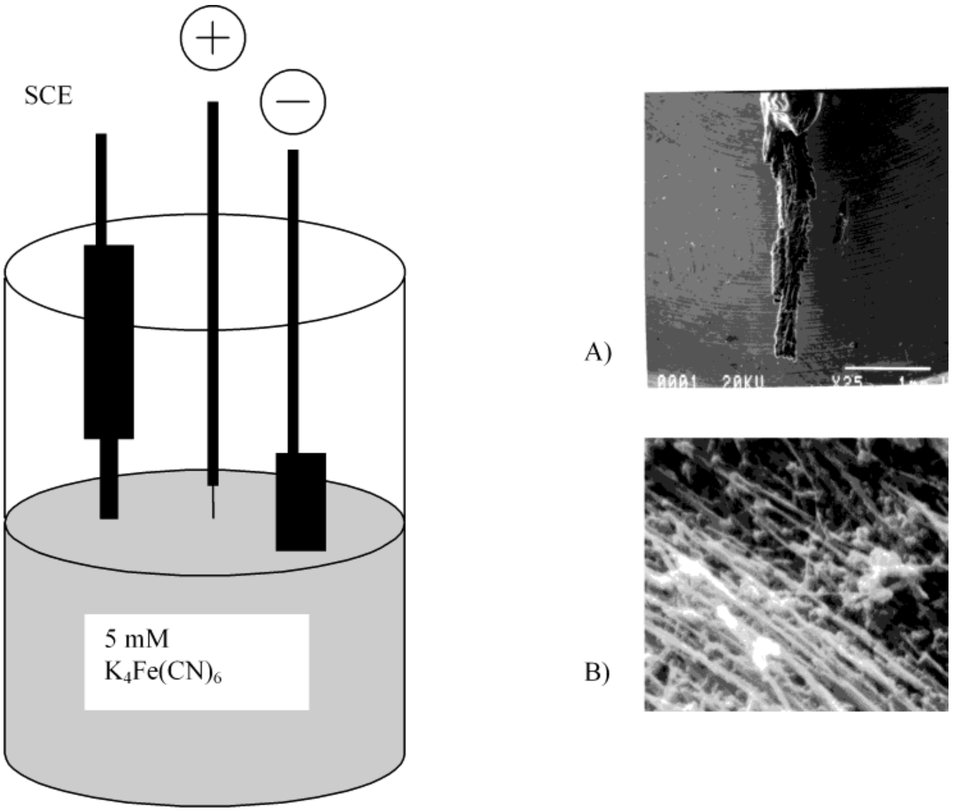

Figure 1. Schematic showing the electrochemical cell used in the experiments for the $K_4Fe(CN)_6$ reaction. (A) Shows the close-up view of the tip of the anode assembly, which is the nanotube bundle. (B) Shows the microstructure of a small area on the porous nanotube electrode; the fibers seen in this image correspond to individual multiwalled nanotubes. There is a range of sizes for the nanotubes (2−25 nm diameter and up to several microns). Closed nanosize polyhedral particles of graphitic carbon can also be seen along with tubes, but the surface structure of the former is essentially the same, exposing only the graphite basal planes.

general the electrodes made of graphitic carbon needs to be pretreated to obtain fast electron-transfer rates during reactions.

Electrodes based on carbon nanotubes are relatively new in electrochemical studies.[9−12] The feasibility of using microelectrodes, based on bundles of multiwalled nanotubes,[9−11] or single electrodes, fabricated from individual multiwalled nanotubes[12] has been demonstrated in the study of electrochemistry. Although nanotubes are produced from the graphite precursor, their structure and topology differ from that of the parent graphite; the structure is tubular and of nanometer dimensions.[13] The surface structure of nanotubes consists entirely of near-perfect atomically smooth graphite basal planes with no dangling bonds or traces of the edge planes. This makes the structure highly surface-specific and differs considerably from that of graphite fibers that expose both basal and prismatic planes on their surfaces. In light of this surface specificity and new topology, and our earlier promising results that showed fast electron transfer during oxygen reduction reactions,[11] we studied the model system of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox electrochemistry using multiwalled carbon nanotube electrodes. The results obtained for this system are consistent with our earlier studies on dopamine (two electron oxidation). Namely, both reactions show Nerstian response and near ideal ET kinetics.

Multiwalled nanotubes (MWNT) are coaxial assemblies of graphene cylinders and have dimensions ranging from 2 to 30 nm in diameter and several microns in length. The electrodes we used were fabricated from arc derived MWNT micro-bundles, which are columns composed of tangled MWNT aggregates.[14] These columns have a highly porous structure containing networks of individual nanotubes. The porous structure and the small dimensions of the nanotubes provide good wetting properties for the solvents and hence good eletrode/electrolyte interface. There is no pretreatment to the electrode involved. The boule that forms on the electrode during the electric arc discharge[14] is broken open, and a micro-bundle of nanotubes is picked out and attached to the end of a copper electrode wire using a conductive silver paint. Typical dimensions of the nanotube bundle electrodes that is used in the experiment corresponds to lengths of ∼0.15 cm and diameters of ∼0.06 cm. The electrode assembly is placed such that only the nanotube bundle comes in contact with the solution (Figure 1).

Figure 2 shows the typical cyclic voltammetric curve of 5 mM potassium ferrocyanide at the carbon nanotube electrode. The ΔE_p is 59 mV at all sweep rates examined (0.02−0.50 V/s) suggesting ideal reversibility at the electrode. It should be noted that the expected theoretical value of ΔE_p falls exactly at 59 mV at 25 °C for the one electron transfer reaction that is purely Nernstian behavior.[15] It is clear that the carbon nanotube electrode is driving the ET reaction faster than any other carbon electrodes surfaces observed to date, with no apparent activation barrier at the electrode

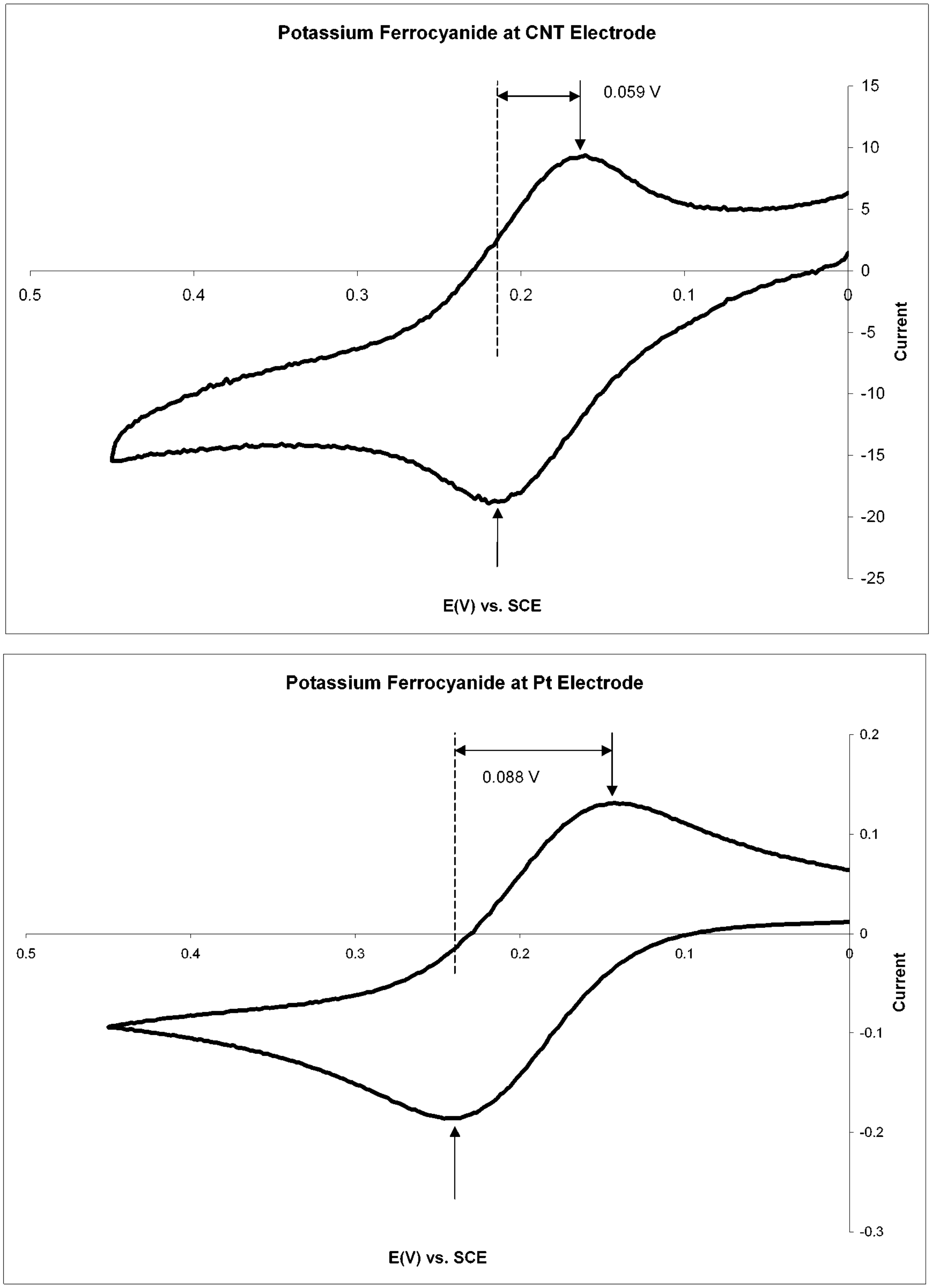

Figure 2. Cyclic voltametric curves of 5 mM $K_4Fe(CN)_6$ on a Pt electrode (bottom) and a carbon nanotube microbundle electrode (top) recorded using a 273 PAR Potentiostat/ Galvanostat. A Pt foil is used as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The anodic peak potential is situated at $E_{pa} = 0.220$ V and the complementary cathodic peak at $E_{pc} = 0.161$ V. The peak potentials did not change with increasing sweep rate up to a high sweep rate of 1 V/s. The current on the *Y*-axis is plotted in units of microamps. Notice the big difference in the background currents for the two electrodes. The apparent electrode areas (calculated from the outer dimensions of the electrodes) of Pt and the nanotube electrodes used in this study are 0.14 cm^2 and 0.009 cm^2 respectively; the real surface area available for electrochemistry for the nanotube electrode could be far greater due to the high porosity of the electrode.

surface. Under identical conditions, we recorded the cyclic voltammetric curve at Pt electrode (see Figure 2), and the ΔE_p is 88 mV. The ET rate constant (k_0) of ~0.5 cm/s was carefully estimated for the ferrocyanide at the nanotube

Table 1. Current Function Data at Microbundle Electrode Showing the Relationship between Scan Rate, Peak Current I_p, and Current Function $I_{Pa}/v^{1/2}$ [a]

sweep rate (mV/s)	i_{pa} (peak current) (μA)	$i_{pa}/v^{1/2}$ (current function) (μA.s$^{1/2}$/(mV)$^{1/2}$)
20	5.49	39.0
50	8.90	40.0
100	11.86	39.5
200	19.89	40.3

[a] The last column is nearly constant. This data shows that it is occurring by semi-infinite linear diffusion.

electrode at 0.02−0.5 V/s and 1 V/s sweep rates. This value represents near ideal behavior for the reversible ET reaction. The result is consistent with results on dopamine oxidation using nanotube electrodes.[10] A ΔE_p value of 30 mV at the nanotube electrodes obtained for the two-electron oxidation of dopamine once again confirms fast electron-transfer characteristics for this electrode. The value reported here for ΔE_p is the best value ever reported for any electrode for the case of our reaction here and for the dopamine oxidation reported earlier[3] and points to the important role the nanotube surface is playing in the electrochemical reaction.

The peak separation observed here applies to semi-infinite linear (i.e., planar) diffusion. The i_p vs $v^{1/2}$ is linear in our experiment (Table 1). In addition, we have not observed any thin layer behavior because the bundle (electrode) dimensions are large compared to diffusion layer thickness (typically about 8×10^{-4} cm at $t = 0.1$ s). The $i_p/v^{1/2}$ is constant, and the i_p/v is not constant. Thin layer behavior would amount to reaction in a confined layer.

Considering that nanotube surfaces are entirely made of the basal planes (which show very slow ET kinetics), it is puzzling that nanotube electrodes provide the highest possible ET rates for the reactions mentioned above. Surprisingly, in their electrochemical, electrodic behavior, nanotubes respond even faster than the graphite edge planes. In discussing earlier studies of the above reaction on carbon fiber electrodes, it was[2] noted that, in general, low modulus fibers exhibit faster ET kinetics than high modulus fibers because the latter have a smaller fraction of exposed edge planes. Several groups have reported the reasons for the large basal/edge plane anisotropy, including the semimetallic character of the basal planes, higher wettability (electrophillic character) of the edge planes and differential conductivity for the two planes.[2] It has been observed, while using individual nanotubes as electrodes, that the nanotubes do not exhibit good wettability. However, when using nanotube based microelectrodes, as in the case here, the electrode has a porous structure (Figure 1b) and is probably well wetted by the solvent/electrolyte medium. In the context of edge vs basal plane reactivity, it must also be remembered that the surface electronic structure of nanotube layers is not entirely graphite basal-plane-like due to the helicity, low dimensionality, and possible topological defects.[16] When the applied external potential is changed, one sweeps through all the singularities in the electronic band structure of the nanotube,[5] which are close to the Fermi energy. As compared to graphite, this higher local-density of states (including surface and defect induced states) could be responsible for favoring faster ET kinetics on nanotube electrodes.

The theoretical description of the electrochemical electron-transfer reaction is complex and different classical and perturbation models have been described in the literature.[17] Just recently, it has been solved using a simple model for electron exchange between a metal electrode and a solvated reactant.[18] The rate constants for either oxidation or reduction can be analytically obtained by taking the limit of the long times in the occupation of the states. The rate constant for electron transfer from the reactant to the electrode is $k_{ox} = \int d\epsilon\ (1 - f(\epsilon,T))w_{ox}(\epsilon)$, where w_{ox} is the rate of electron transfer from an occupied level of the reactant to an empty level of the electrode. This energy-resolved rates are given in ref 16 in terms of the density of available states, the electron-resonance width and the strength of the coupling to the phonon bath. The activation energy for the reaction decreases with increasing the electronic interaction width. The structure of the tubes, as well as their different local density of states, might be responsible for the increase of the electronic-energy interaction width (as discussed above). Also, the better wetting properties of carbon nanotube bundles, as compared to other carbon-structures[19] and individual nanotube electrodes,[12] could also be responsible for this enhanced ET rate, from the creation of an ideal wetted solid-electrolyte interface. We are currently performing more studies in order to address the electron-transfer mechanism in carbon structures.

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