

Interfacial electron transfer kinetics at single CCVD multiwalled carbon nanotubes

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Abstract

The understanding of charge transfer processes between nanomaterials and solvated molecules is a long-standing goal that concerns many applications, as diverse as biosensing, catalysis, energy production and storage, etc. Despite the enormous amount of data on electrochemistry with CCVD multiwalled carbon nanotubes, there remains a controversy about the origin of mechanisms involved in the charge transfer kinetics. Dealing properly with this problem necessitates controlling the geometry of the device under test to analyze the quasi-reversible regime and discriminate between kinetic and diffusion effects in the steady state [1]. The faster the reaction, the smaller the device surface.

We report here on new experiments of redox outer-sphere electron transfer between single multiwalled carbon nanotubes and two species, 1-1'-ferrocene dimethanol (FeDM) and $\text{Ru}(\text{NH}_3)_6^{3+}$, in aqueous solutions. To minimize contamination effects, we have elaborated a new process where single MWCNTs are connected to etched gold tips by fast electrical breakdown, the adhesion being ensured by van der Waals forces only (fig. 1). After attachment of the MWCNT, the electrode is mounted on a micromanipulation stage under optical control. Cyclic voltammograms and chronoamperometry curves were recorded at various immersion depths in a home-made liquid cell. MWCNTs show quasi-reversible quasi-steady-state reactions with FeDM and $\text{Ru}(\text{NH}_3)_6^{3+}$, and kinetic parameters are estimated using simple geometrical models. CVs were analyzed in the framework of the Butler-Volmer kinetic equation,

$$i = \frac{i_{\text{lim}}}{\frac{1}{\alpha} \left(1 + e^{-\frac{F(E-E^0)}{RT}} \right) + \frac{1}{L^*} e^{-\frac{F(1-\alpha)(E-E^0)}{RT}}}, \quad (1)$$

where i_{lim} is the diffusion limited current, which is proportional to the area of active sites, F the Faraday constant, R the molar gas constant, E^0 the formal potential of the redox-couple, α the transfer coefficient, and L^* the dimensionless heterogeneous rate constant that depends on geometry and k^0 [3]. It appears that MWCNTs behave as partially blocked microcylinders, with moderate heterogeneous rate constant ($\langle k^0 \rangle = 0.2$ cm/s). An anomalous transfer coefficient (>0.7) is measured systematically (fig. 2). We discuss the origin of this behavior in the framework of microscopic models adapted to nanometer-sized electrodes [3].

References

- [1] Bond AM, Oldham KB, Zoski CG, Anal. Chim. Acta 216 (1989) 177.
- [2] Amatore CA, Deakin MR, Wightman RM, J. Electroanal. Chem. 206 (1986) 23.
- [3] Liu Y and Chen S J., Phys. Chem. C 116 (2012) 13594.

Figures

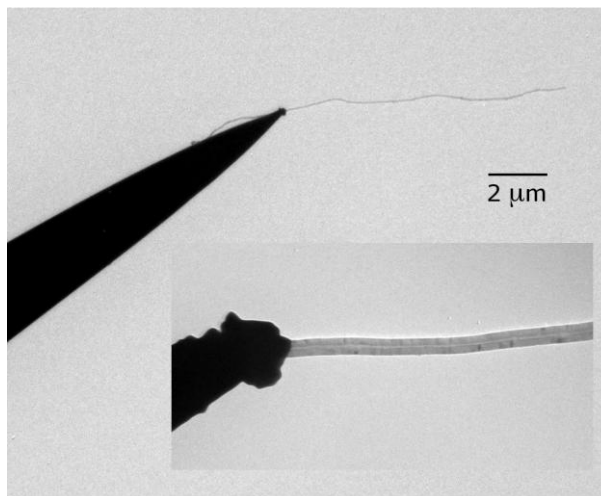


Figure 1. TEM image of a 70-nm diameter MWCNT connected to an etched gold tip

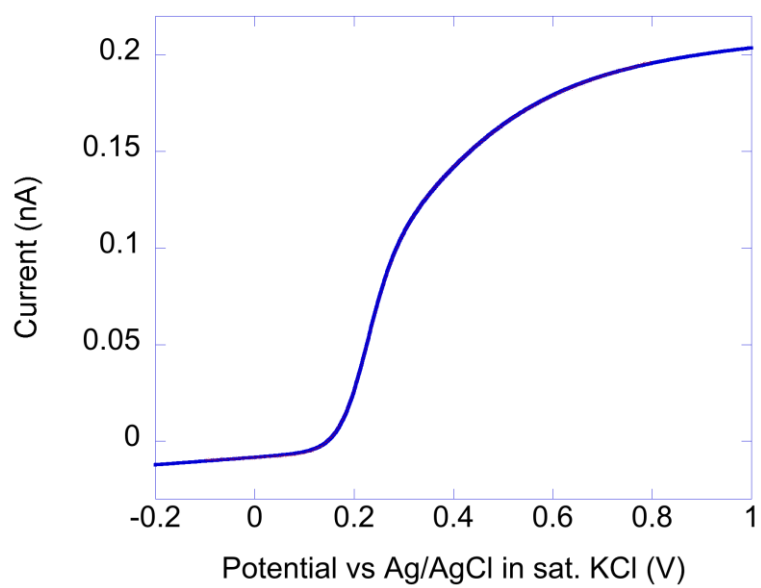


Figure 2. Cyclic voltammogram of a 60-nm MWCNT, immersion depth 4 μm, in 1mM FeDM + 0.5 M KCl. Scan rate 0.1 V/s. Data were fitted by Butler-Volmer equation (blue line masks data points). The rate constant was 0.4 cm/s and transfer coefficient 0.84.