

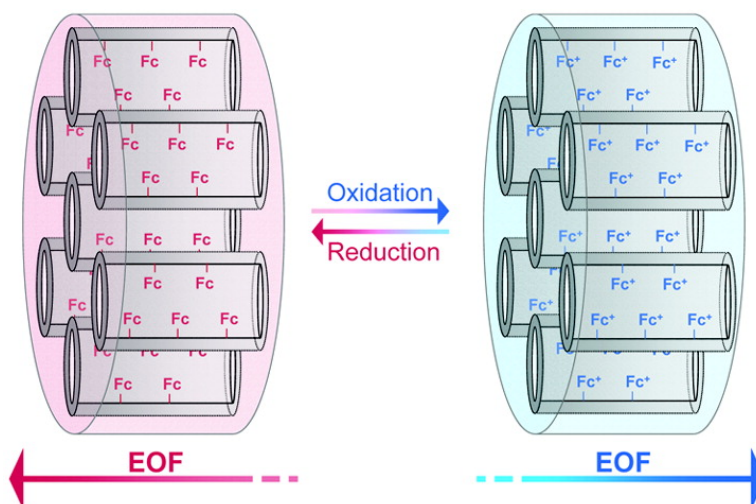
Communication

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Redox Modulation of Electroosmotic Flow in a Carbon Nanotube Membrane

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Electroosmotic flow (EOF) is used to manipulate solutions in capillaries and microfluidic devices¹ and more recently in the nanotubes of a carbon nanotube membrane (CNM).² In all of these applications it is important to control both the rate and direction of EOF, independently of the electric field that drives EOF. For this reason, there has been considerable recent effort devoted to developing ways of modulating the rate and direction of EOF.^{3–7} We describe here a new method, and we use the CNM system² to demonstrate this method.

This new method entails coating the inside walls of the carbon nanotubes within the CNM with redox-active polymer films. The redox polymer, poly(vinylferrocene),⁸ can be reversibly electrochemically switched between an electrical neutral and a polycationic form. This provides a way for controlling both the magnitude and the sign of the surface charge on the nanotube walls, which in turn allows for control of both the rate and direction of EOF through the CNM.

The Helmholtz–Smoluchowski equation² provides a basis for understanding how the velocity of EOF, v_{eo} , might be modulated.

$$v_{eo} = -\epsilon\zeta J_{app}\rho/\eta \quad (1)$$

In this equation, ϵ , ρ , and η are the permittivity, resistivity, and viscosity of the electrolyte solution being driven by EOF, J_{app} is the applied current density in this solution, and ζ is the zeta potential of the surface in contact with the solution; e.g., the nanotube, capillary, or microfluidic-channel wall.

Equation 1 shows that the magnitude and sign (direction) of v_{eo} are related to the magnitude and sign of the current density, and this provides a traditional way for modulating EOF. Equation 1 also shows that v_{eo} is related to ζ , which is in turn related to the magnitude and sign of the surface charge density (σ)

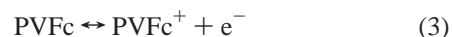
$$\zeta = \frac{\sigma\kappa^{-1}}{\epsilon} \quad (2)$$

where κ^{-1} is the Debye length at the solid/electrolyte solution interface.² Equation 2 suggests that, if the magnitude and sign of σ can be changed at will, the rate and direction of EOF can be modulated. Our new redox-polymer-based method allows for reversible control over both the sign and magnitude of σ .

The CNMs were prepared by using chemical vapor deposition to line the pore walls in a nanopore alumina template with carbon nanotubes.² This yields a free-standing membrane with walls coated with carbon nanotubes that span the thickness of the membrane ($\sim 60 \mu\text{m}$). The faces of the membrane are also coated with carbon, although the pores at the membrane surface are not blocked.² These carbon-surface films allow us to make electrical contact with the nanotubes in the membrane. The alumina template was a filter (Anopore, Whatman) with 200-nm-diameter pores. The inside diameter of the carbon nanotubes was 120 nm.

The redox polymer poly(vinylferrocene) (PVFc) can be electrochemically synthesized as an ultrathin film on an electrode surface from the monomer, vinylferrocene.⁸ This method was used to coat the inner walls of the carbon nanotubes with PVFc. The CNM working electrode was immersed into a solution that was 8 mM in vinylferrocene and 50 mM in Bu_4NClO_4 in degassed CH_3CN . Polymerization was done voltammetrically by scanning the potential of the CNM between +1.0 and -2.8 V vs a Ag/AgCl reference. The scan rate was 10 mV s^{-1} .

The electrochemistry of the PVFc within the carbon nanotube/PVFc (CN/PVFc) membrane can be represented as



Cyclic voltammetry using the CN/PVFc membrane as the working electrode clearly shows this reversible redox reaction (Figure 1). The area under the voltammogram provides the moles of PVFc deposited along the nanotube walls. Ideally, we want monolayer coverage. From the inner surface area of the carbon nanotubes, the number of moles of PVFc in the membrane, and the number of moles of PVFc equivalent to a monolayer,⁸ we calculate that $\sim 40\%$ of a monolayer is deposited within the nanotubes. This calculation assumes that all of the carbon nanotubes in the membrane are redox active and contain PVFc, and this may not be the case. However, these data clearly show that we have sufficient redox-active PVFc in the nanotubes.

EOF was driven across the CN/PVFc membrane as described previously.² Briefly, the membrane (0.713 cm^2) was mounted between the two halves of a U-tube permeation cell, and the half-cells were filled with 0.01 M KClO_4 adjusted to pH 3.5 with HClO_4 .⁹ A Pt electrode was placed into each half-cell solution, and a galvanostat was used to apply a constant current between these electrodes to drive EOF through the CN/PVFc membrane. One of the half-cell solutions was also 5.0 mM in the small, electrically neutral, chromophore phenol. The magnitude of v_{eo} was determined via an analysis of the phenol flux with and without the applied transmembrane current.²

The novel feature of these experiments is that prior to determining v_{eo} a known potential was applied to the CN/PVFc membrane to totally oxidize, partially oxidize, or totally reduce the PVFc within the nanotubes (eq 3). After equilibration ($< 30 \text{ s}$) the membrane was then removed from potentiostatic control, and v_{eo} was measured with the PVFc in that selected oxidation state.

Figure 2 shows plots of v_{eo} vs applied current density for the two extremes: $+0.7 \text{ V}$, where all the PVFc is present as PVFc^+ and -0.2 V , where all the PVFc is present as uncharged PVFc. Equation 1 predicts that v_{eo} is linearly related to J_{app} , and this is observed experimentally for both oxidation states. ζ can be obtained from the slopes of such plots (eq 1).² When the polymer is in the PVFc^+ state, the excess positive surface charge on the nanotube walls should result in a positive ζ , and this is observed experimentally ($\zeta = +17.2 \text{ mV}$).

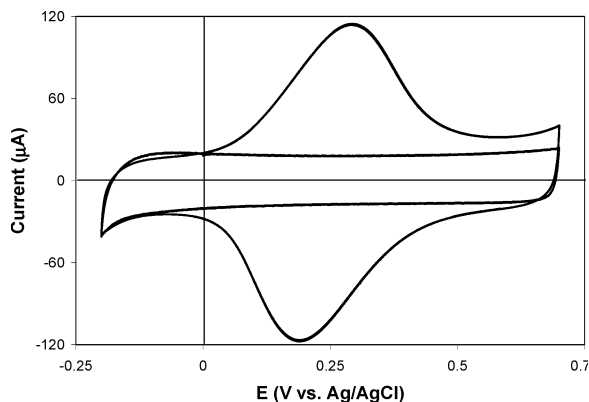


Figure 1. Cyclic voltammograms for the CNM and the CN/PVFc (upper curve) membrane. Scan rate = 10 mV s⁻¹. Electrolyte = 0.1 M KClO₄.

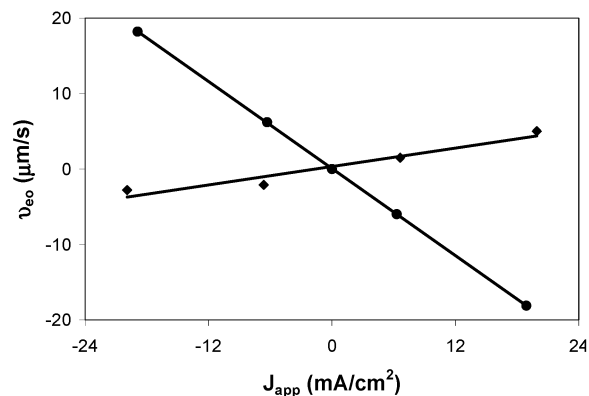


Figure 2. Plots of electroosmotic flow velocity vs applied current density for totally oxidized (●) and totally reduced (◆) CN/PVFc membranes.

When the polymer is reduced (PVFc form) there should be no excess surface charge, and ζ should be zero. However, a small negative ζ was obtained for the totally reduced polymer (Figure 2). This may be because the CNM with no PVFc has a small negative ζ at this pH.² In addition, there may be residual anionic sites on the PVFc due to air oxidation of the polymer. The negative ζ for the membrane when the polymer is completely reduced is fortuitous because it allows us to have EOF in one direction through the membrane when the polymer is oxidized and to have EOF in the opposite direction (although at a lower rate) when the polymer is totally reduced (Figure 2). When the polymer is totally oxidized, this residual anionic surface charge is more than compensated by the positive charge of the PVFc⁺.

Finally, in addition to the two extremes—all PVFc⁺ at +0.7 V or all PVFc at -0.2 V—the Nernst equation tells us that the ratio of moles of PVFc⁺ to the moles of PVFc can be adjusted to any desired value by applying potentials that are intermediate between these two extremes. This should provide a way to adjust the excess positive surface charge, and thus the electroosmotic flow rate, to any value between the +0.7 and -0.2 V limits. We have proven this point by measuring v_{eo} after applying to the CN/PVFc membrane various potentials between these extremes. Again, the potential was applied until equilibrium had been achieved, the membrane was released from potentiostatic control, and v_{eo} was measured. The data obtained were processed as a plot of ζ , which

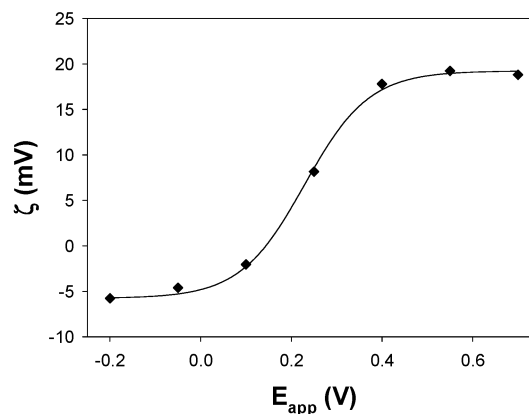


Figure 3. Plot of ζ vs potential applied to the CN/PVFc membrane.

as eq 2 shows is directly proportional to v_{eo} , vs potential applied to the CN/PVFc membrane (Figure 3).

Figure 3 shows that ζ increases from its negative limit when the potential applied to the membrane is more than 0 V and increases continuously until an applied potential of $\sim +0.5$ V is reached. This response is in good agreement with the cyclic voltammogram (Figure 1) where we see that oxidation of the polymer to produce PVFc⁺ starts at potentials more than 0 V, and oxidation is complete when the potential reaches $\sim +0.5$ V. This agreement is observed because the voltammetric scan rate is low enough that equilibrium in the PVFc film is achieved at all applied potentials.

We have demonstrated a new approach for modulating EOF. This method should be applicable to any device or system using EOF, provided a redox polymer can be coated along the flow channel and the walls of the flow channel are electronically conductive, so that the redox state of the polymer can be changed. In some ways this approach is similar to a field-effect concept³ in which a much larger potential (>50 V) was applied to an electronically conductive phase coated on the outside of an electronically insulating microfluidic channel.⁴ The advantage of this non-Faradaic approach is that the channel itself does not need to be electronically conductive. The advantage of our approach is that much smaller voltages are needed and the voltage must be applied for only a few seconds to change the oxidation state of the polymer. Hence, in principle, redox modulation could be implemented with only a small battery for surface charge control.

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