

## Nanoparticle Film Charging—Ion Rectified or Ion Limited?

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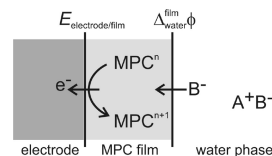
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Redox active thin films are of relevance to a variety of applications such as sensors and optoelectronics based on conductive polymers or quantum-dot solids.<sup>1</sup> The injection/ejection of charge compensating counterions into such films can be a critical aspect of device performance. Here we consider how differences in ion solvation in the film versus the electrolyte phase can control the apparent redox properties of model electroactive thin films. Ion transfer across the film/solution interface has received little attention to date, and here we will demonstrate how it can effectively shut off the redox response of nanoparticle films.

Thiol protected gold nanoparticles, so-called monolayer protected clusters (MPCs) can be considered as multivalent redox species.<sup>2</sup> Experimentally, the oxidative charging of hydrophobic MPC thin films coated on electrodes and immersed in aqueous solution depends on the nature and concentration of the aqueous electrolyte anion.<sup>3</sup> The onset potential for the first oxidation is dependent on the hydrophobicity of the anion and shifts to more negative potentials with increasing anion hydrophobicity in the following order:  $\text{NO}_3^- < \text{BF}_4^- < \text{ClO}_4^- < \text{PF}_6^-$ . This apparent anion rectifying effect has been interpreted in terms of ion association where the oxidized MPCs form ion pairs with the electrolyte anion.<sup>3</sup> The shift in onset potential would then be due to the differing MPC–anion association constants, with more hydrophobic ions binding more strongly.<sup>3</sup> This thermodynamic interpretation can reproduce most of the experimental observations but fails to address why similar rectification has never been observed for comparable MPC films in organic solvents in the presence of the same electrolyte anions.<sup>4</sup>

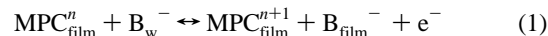
To date, the immiscible interface formed upon contacting the hydrophobic MPC film and the aqueous phase has not been considered. Energy is required to transfer an ion across this boundary and this is related to the difference in ion solvation in the respective media.<sup>5</sup> The MPC-film-modified electrode immersed in aqueous electrolyte is analogous to the thin-film-modified electrode pioneered by Scholz, Compton and co-workers where a thin film of organic solvent containing an electroactive redox species is spread on a graphite electrode and immersed in aqueous electrolyte solution.<sup>6</sup> With this experimental arrangement, it has been demonstrated that electron transfer at the electrode/film interface is coupled to ion transfer across the film/solution interface. Because of the electroneutrality condition, the two processes occur simultaneously and the redox reaction can only proceed together with the injection or expulsion of the counterion.<sup>6</sup> The experimental half-wave potential is determined by both the redox reaction and the ion-transfer reaction.<sup>6</sup> The MPC film is essentially a thin organic phase as illustrated schematically in Figure 1. The particles are multivalent redox centers that undergo electron transfer at the metal electrode surface while the film/solution interface is a solvation barrier to the transfer of charge compensating ions into the film. In this model, the MPC charging at the electrode surface is not



**Figure 1.** Schematic illustration of coupled electron and ion transfers for the oxidative charging of hydrophobic MPC films in aqueous solution.

possible without the transfer of counterions across the film/solution interface to preserve the electroneutrality of the film.

The overall electrode reaction for the oxidation of film MPCs in an aqueous electrolyte  $\text{A}^+\text{B}^-$  can be written as follows:



The charging of the MPC at the film/electrode interface serves as the driving force for ion transfer across the film/solution interface. The overall reaction couples these processes, which occur simultaneously and cannot be separated. As the film is conductive, ohmic loss in the film is not limiting.<sup>6</sup>

The potential difference established across the film/solution interface  $\Delta_w^{\text{film}}\phi$  is dependent on the relative hydrophobicity of the constituent anions and cations.<sup>5</sup> Charge transfer across this interface is not a redox process and is simply a measure of the relative solvation properties of the transferring ionic species in each phase.<sup>5</sup>  $\Delta_w^{\text{film}}\phi$  can be written as follows:

$$\Delta_w^{\text{film}}\phi = \phi^{\text{film}} - \phi^w = \Delta_w^{\text{film}}\phi_B^{\text{of}} + \frac{RT}{F} \ln \frac{[\text{B}_{\text{film}}^-]}{[\text{B}_w^-]} \quad (2)$$

where  $\Delta_w^{\text{film}}\phi_B^{\text{of}}$  is the formal transfer potential for the anion, and  $[\text{B}_{\text{film}}^-]$  and  $[\text{B}_w^-]$  are the film and solutions concentrations, respectively. As discussed by Scholz, the applied potential  $E$  is the sum of the potential drop across the electrode/film and film/solution interfaces<sup>6a</sup>

$$E = E_{\text{electrode}/\text{water}} = E_{\text{electrode}/\text{film}} + \Delta_w^{\text{film}}\phi \quad (3)$$

At equilibrium, overall reaction 1 can be described by the Nernst equation:

$$E = E^{\text{of}} + \Delta_w^{\text{film}}\phi_B^{\text{of}} + \frac{RT}{F} \ln \frac{[\text{MPC}^{n+1}][\text{B}_{\text{film}}^-]}{[\text{MPC}^n][\text{B}_w^-]} \quad (4)$$

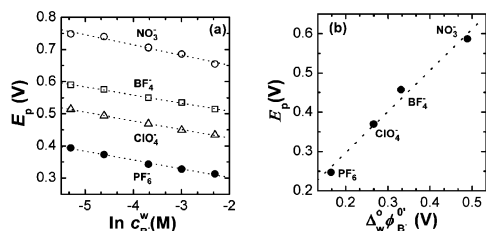
where  $E^{\text{of}}$  is the formal potential for MPC charging and  $[\text{MPC}^n]$  and  $[\text{MPC}^{n+1}]$  are the concentrations of the charged MPC species inside the film. We can rewrite eq 4 in terms of the half-wave potential

$$E_{1/2} = E^{\text{of}} + \Delta_w^{\text{film}}\phi_B^{\text{of}} + \frac{RT}{F} \ln \left( \frac{2n+1}{2} [\text{MPC}]_{\text{tot}} \right) - \frac{RT}{F} \ln [\text{B}_w^-] \quad (5)$$

where  $[\text{MPC}]_{\text{tot}}$  is the total nanoparticle concentration in the film.

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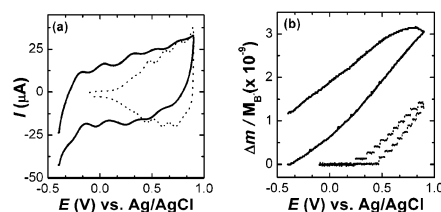


**Figure 2.** (a) Dependence of the MPC film first oxidation peak potential on the concentration of the aqueous electrolyte anion  $\text{B}^-$ :  $\text{NH}_4\text{PF}_6$  (●),  $\text{NH}_4\text{ClO}_4$  (△),  $\text{NH}_4\text{BF}_4$  (□), and  $\text{NH}_4\text{NO}_3$  (○) (Na acetate was added to keep an overall concentration of 0.1 M in all cases). (b) Dependence of MPC oxidation peak potential on the formal anion transfer potential across the water/dichlorobenzene interface of the aqueous anion used.

Thus, a 10 fold increase in the anion concentration should shift the measured  $E_{1/2}$  by 59 mV in a negative direction. This predicted dependence is identical to that in the ion pairing model for 1:1 binding between the oxidized MPC and the aqueous anion.<sup>3</sup> As can be seen in Figure 2a, the prediction is in complete agreement with the dependence of experimental peak potentials on anion concentration for a MPC-film-modified gold electrode in the presence of various anions and identical to literature reports for comparable particle films.<sup>3,7</sup>

Equation 5 also shows how the measured  $E_{1/2}$  depends on the nature of the aqueous anion via the transfer potential term. Generally, the formal transfer potential values decrease as anion hydrophobicity increases and vice versa for hydrophilic ions. Consequently the oxidation of the MPC in the film will be shifted to more negative potentials when the lipophilicity of the anion increases.<sup>5</sup> Thus, to verify that the anion dependence apparent in Figure 2a is really ion transfer limited and not ion rectified, the charging onset potentials were compared to calculated  $\Delta_w^{\text{film}} \phi_B^o$  values using Gibbs energies of transfer between water and dichlorobenzene (DCB) ( $\Delta_w^o \phi_i^o = \Delta G_{\text{tr},i}^{0,w \rightarrow o} / z_i F$ ).<sup>5,8</sup> While an MPC film is not strictly comparable to simple solvents such as DCB, differences in Gibbs energies will be of the right magnitude and we should see the same order in the position of the onset potentials. Calculated standard transfer potentials for the four most commonly used anions were 165 mV ( $\text{PF}_6^-$ ), 266 mV ( $\text{ClO}_4^-$ ), 331 mV ( $\text{BF}_4^-$ ), and 489 mV ( $\text{NO}_3^-$ ).<sup>8</sup> This is the same order that is seen experimentally (Figure 2b). The plot of peak potentials obtained in the presence of each ion (extrapolated to  $\ln[\text{B}_w^-] = 0$ ) versus the standard ion transfer potentials given in Figure 2b is linear with a slope of 1 as predicted by eq 5.

Thus, the onset potential of the film charging is controlled by the polarizability of film/water interface. The observed response should be highly dependent on both the solvent and the hydrophobicity of the aqueous phase anion. A simple experiment was conducted to study the latter. The cyclic voltammetry (CV) responses obtained for a drop-cast film of hexanethiol protected MPCs on a gold quartz crystal microbalance (QCM) electrode in aqueous solution containing a moderately hydrophilic anion  $\text{PF}_6^-$  and a very hydrophobic anion, pentafluorotetraphenylborate ( $\text{TPBF}_{20}^-$ ), are compared in Figure 3a (full experimental details are in Supporting Information). The  $\text{PF}_6^-$  case shows a clear onset for charging as it does not transfer until  $\Delta_w^{\text{film}} \phi > \Delta_w^{\text{film}} \phi_{\text{PF}_6^-}^o$ . Until this criterion is fulfilled, electron transfer is also shut off and the measured current is zero. In contrast, for the  $\text{TPBF}_{20}^-$  case, there is no onset potential for MPC charging and peaks are apparent throughout the available potential window. The response is comparable to that obtained for dispersed particles in dichloroethane (Supporting Information).  $\Delta_w^{\text{film}} \phi_{\text{TPBF}_{20}^-}^o \ll 0$  and  $\Delta_w^{\text{film}} \phi > \Delta_w^{\text{film}} \phi_{\text{TPBF}_{20}^-}^o$  for all applied potentials within the available potential window. Thus, hydrophobic  $\text{TPBF}_{20}^-$  transfers into the film at all



**Figure 3.** (a) CVs recorded for an MPC-film-modified gold QCM electrode immersed in aqueous solution containing 20 mM  $\text{NH}_4\text{PF}_6$  (dotted line) or  $\text{LiTPBF}_{20}$  (full line) and 80 mM sodium acetate. Scan rate = 50  $\text{mV s}^{-1}$ ; (b) mass changes recorded simultaneously during the CV experiments divided by the molecular weight of the anion used.

interfacial potentials. This is confirmed by the mass changes observed in the in situ QCM measurements recorded simultaneously given in Figure 3b. Mass changes are seen throughout the window for  $\text{TPBF}_{20}^-$  and only after the onset potential has been reached for  $\text{PF}_6^-$ .

This ion transfer limited model can account for the dependence of MPC oxidative charging on the nature and concentration of the aqueous anion without invoking any interaction between the MPC and the counterion as in the association model. It can quantitatively explain shifts in apparent film redox potentials with differing anions. Also, the absence of rectification when the film is immersed in organic solvents with identical anions is logical because of the low solvation barrier for counterion transfer. This study highlights the role of counterion solvation on the response of thin-film-modified electrodes. We show that the observed behavior can be better understood as ion limited rather than ion rectified.

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**Supporting Information Available:** Voltammetry of the particles dispersed in organic solvent and additional experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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