



Theoretical voltammetric response of electrodes coated by solid polymer electrolyte membranes



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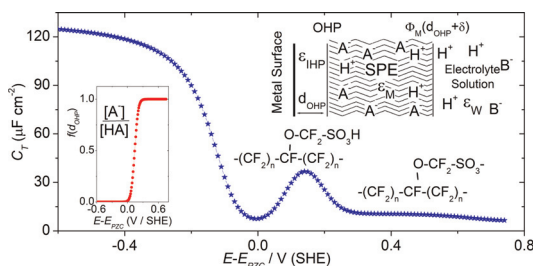
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HIGHLIGHTS

- Discretized model for an interface of covered electrodes.
- Two limiting behaviors are captured: double-layer and conductive interfaces.
- Additional phenomena are included easily: acid/base equilibrium, ion mobility.
- The model provides explanations to observed phenomena that is vaguely explained in the literature.
- Implications on electrodes in fuel cells are given and it opens avenues to understand and design such systems.

GRAPHICAL ABSTRACT



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ABSTRACT

A model for the differential capacitance of metal electrodes coated by solid polymer electrolyte membranes, with acid/base groups attached to the membrane backbone, and in contact with an electrolyte solution is developed. With proper model parameters, the model is able to predict a limit response, given by Mott–Schottky or Gouy–Chapman–Stern theories depending on the dissociation degree and the density of ionizable acid/base groups. The model is also valid for other ionic membranes with proton donor/acceptor molecules as membrane counterions. Results are discussed in light of the electron transfer rate at membrane-coated electrodes for electrochemical reactions that strongly depend on the double layer structure. In this sense, the model provides a tool towards the understanding of the electro-catalytic activity on modified electrodes. It is shown that local maxima and minima in the differential capacitance as a function of the electrode potential may occur as consequence of the dissociation of acid/base molecular species, in absence of specific adsorption of immobile polymer anions on the electrode surface. Although the model extends the conceptual framework for the interpretation of cyclic voltammograms for these systems and the general theory about electrified interfaces, structural features of real systems are more complex and so, presented results only are qualitatively compared with experiments.

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1. Introduction

Modification of electrode surfaces by coating them with a film of a selected chemical moiety to modify the physical, electrochemical and/or optical properties of the unmodified substrate has been a very active area in electrochemistry in recent years [1,2]. A number of reviews, discussing preparation, characterization, and electrochemical response of chemically modified electrodes, are available [1]. The film can be an irreversible adsorbed (or covalent attached) monolayer or a polymeric (or inorganic) multilayer coating. Hence, it is important to distinguish between physical adsorption, where the film is attracted to the surface via electrostatic or non-electrostatic interactions, and chemical adsorption, where a part of the molecule is chemically bound (grafted) to the surface [3].

Modified electrodes are attractive mainly in electrocatalysis, but they could be employed in electrochromic, molecular electronic and active display devices, in analytical sensors, reference electrodes or to protect the underlying substrate from corrosion or chemical attack [1]. In addition, they have been used to characterize electron and mass transfer processes in polymers and other materials, giving insights into how surface structures can be designed to carry out specified reactions or processes [1,4]. Specifically, electrodes coated with ion selective membranes based on solid polymer electrolytes (SPE) are used in many electrochemical systems, where selective separation of ion fluxes is required, like proton membrane fuel cells (PMFC) [5–8], wastewater treatment equipment [9,10] and electrochemical sensors [1,11,12]. SPE are usually ionomers, i.e. polymers with ionic groups (e.g., SO_3^- , CO_2^- , PO_3^-) on the side chains [3,4,8]. The most extensive investigated ionomer is Nafion[®], a polymer of tetrafluoroethylene (PTFE) in which the elementary blocks are $-(\text{CF}_2)_n-\text{CFR}-(\text{CF}_2)_m-$, with $\text{R} \equiv -\text{O}-\text{CF}_2-\text{SO}_3^-$ as the side chain [5,6,8,13].

Several theoretical studies have described the equilibrium adsorption of neutral and charged polymers to surfaces and interfaces. They include the analysis of polymer/surface interactions, solvent quality, surface characteristics and polymer structures [3,14,15]. Most of these works have used scaling, mean-field, self-consistent field or molecular theories [2,7,15–22]. For an extensive review see the work of Netz and Andelman [3,14]. Nevertheless, few theoretical studies have focused on the relation between the modified electrode electrochemical properties and the molecular organization within the layer [2,16,21–30]. Besides, the molecular complexity of the problem forces much of this theoretical work to rely on phenomenological ideas and excludes specific film molecular characteristics [1,23–29], providing a partial description of the electrochemical processes [16]. Additional work is needed towards a full understanding of interfacial phenomena at these integrated electrochemical systems.

The structure and dynamics of the electrode/SPE interface, i.e., the formation of the electrical double layer (EDL), has been usually described by employing either models in analogy with the conventional Mott–Schottky (MS) model of charge transfer and band bending near a semiconductor/metal interface [31,32], by considering the restricted mobility of the ionic groups on the side chain attached to the polymer backbone [1,30,33–38], or by means of an extended version of the classical Gouy–Chapman–Stern (GCS) model [39–41], in which the position of SPE charges are considered discrete [42]. These models give similar interfacial differential capacitance responses as a function of the electrode potential [42], and a square-root asymptotic scaling of the total charge with diffuse layer voltage for the charged diffuse layer, composed by immobile membrane ions [34–38]. However, in most of these systems there is at least one protonable species and, therefore, the

properties of the modified electrode should depend on the pH of the solution in contact or adjacent to the electrode [2].

In contrast, there are different theoretical approaches to calculate the interfacial potential distribution (IPD) and the reversible voltammetric, or chronoamperometric, response of coated electrodes by an irreversible monolayer or submonolayer. These films are either electroactive, or electrochemically inert compounds of molecular acids or bases, confined to the surface electrode, such as Langmuir–Blodgett (LB) and self-assembled monolayers (SAMs) [16,43–50]. For SAMs, sometimes models predict an acid/base equilibrium shifted by changes in solution conditions and the electrode potential, coupled with the molecular organization of the film [16,43,46,47,50]. In addition, under certain conditions, a maximum in capacitance–potential curves is expected, due to the dissociation of the acid at increasing electrode potential. These predictions have been validated by cyclic voltammetry (CV) [44,47,51], electrochemical impedance spectroscopy (EIS) [52–54], Fourier transform infrared external reflection (FTIR-ERS) [51] and surface enhanced Raman scattering spectroscopy (FT-SERS) experiments [55].

In this work, a model for the electrode/SPE interface in contact with an electrolyte solution is proposed, in which the membrane contains acid/base groups attached to its polymer backbone. The model includes both a thermodynamic treatment of the acid/base equilibrium between charged groups inside the ionomer and a discrete description of the charge position, taking into account the different mobility of polymeric ionic groups and counterions inside the membrane. Similar to the case of adsorbed monolayers, and even in absence of specific adsorption of polymeric anions on the electrode surface, an asymmetrical maximum in current–potential curves may appear. This asymmetric response is consequence of changes in the fraction of ionizable groups, due to changes in solution conditions and the applied electrode potential.

2. Electrochemical model for the interface

For the description of the interface, the model assumes a flat metal electrode of area, A , located at $x=0$. An electro-inactive SPE, physically adsorbed, of thickness δ (m) and with a dielectric constant ϵ_M covers the electrode. The SPE membrane lays at the outer Helmholtz plane (OHP), which is the plane of closest approach for the fully solvated membrane and bulk ions, set at a distance d_{OHP} (m) from the surface. At the inner Helmholtz plane (IHP), the inner layer of the electrode/SPE interface between the electrode and OHP ($0 < x < d_{\text{OHP}}$), there is a layer of water molecules, whose properties are different from the bulk water. This inner water layer has a low dielectric constant, $\sim 3 \leq \epsilon_{\text{IHP}} \leq 15$ [46], and a thickness d_{OHP} . The potential drop in this region is described by a linear profile [1] (see Fig. 1).

At $x=d_{\text{OHP}}+\delta$, the outer surface of the membrane is in equilibrium with a large volume of a $z:z$ symmetrical electrolyte solution of concentration n (mol cm^{-3}) and dielectric constant ϵ_W . Therefore, the model considers two interfaces: the metal/SPE and the SPE/solution interfaces. In the first case, an electrical diffuse layer, of size L_{EDL} (m), spreads inside the membrane as a result of the electrode potential, Φ_E (V) [33]. In the second case, an electrical potential difference is established between the membrane and the solution, Φ_{EQ} (V). This difference arises from an equilibrium balance of the selective charge exchange across the interface, usually called Donnan equilibrium [1,56,57], and it exists even in absence of the metal/SPE interface. Because of that, there is a continuous IPD that diffuses over distances of order $1/K_M$ on both sides of the membrane/solution interface, where local electro-neutrality no longer holds [56,57]. The parameter K_M (m^{-1}) is known as the membrane DebyeHückel parameter defined by

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