Development and applications of electrochemistry at soft interfaces and nanoparticles

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After discussing the fundamental issue of charge distributions at polarized interfaces, we present the concept of the “Discrete Helmholtz Model” for liquid-liquid interfaces and also for other non-metallic interfaces. We introduce the newly discovered ionosomes, which are nano liquid-liquid interfaces. We finish by presenting our work of water splitting using redox electrocatalysis in a batch mode, using an aqueous redox battery and finally using molecular electrocatalysts.

Introduction

Understanding what happens when an electronic conductor, such as a metal, is immersed in an electrolyte, is one of the oldest challenges of electrochemistry.

Contact electrification between two solids discovered in the XVIIIth, and known today as triboelectricity, had open the way to experimental electrochemistry, and the well-known experiments on frogs by Luigi Galvani are perhaps the first examples of observing what happens when a metal wire is inserted in a muscle.

In 1879 in a paper entitled: “About some laws of the distribution of electrical currents in biological conductors with application to the animal-electrical experiments”, Hermann von Helmholtz had suggested that an excess of electronic charges on a metal must be compensated by an excess of ionic charges at the interface on the electrolyte side, to maintain the whole interface as neutral and thereby forming an interfacial capacitor as shown in Figure 1.

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dynamics, this model had been revisited independently by Louis Gouy\textsuperscript{2}) in France and David Chapman\textsuperscript{3}) in England to propose what is known today as the Gouy-Chapman model, where the ionic distribution in solution is assumed to be diffuse within a certain layer thickness (few nanometres). By definition, the electronic charge on the metal was also assumed to be diffuse at least in the plane of the interface.

In 1928, Otto Stern\textsuperscript{4}) proposed to merge the two models leading to what is known today as the concept of the Stern layer as shown in Figure 2.

Fig. 2. Potential distribution. Top: Helmholtz layer and diffuse layer for a positively charged electrode. Bottom: In the presence of specific adsorption, the positive charge on the electrode can be overcompensated by negatively charged adsorbed anions, known today as the Stern layer, such as the diffuse layer has an excess of cations. Adapted from Ref. 4.

During the first half of the XX\textsuperscript{th} century, most of the experimental studies were carried out at the mercury-electrolyte interface using the mercury drop electrode, as the renewable electrode surface was highly reproducible. This technique of recording the current on a dropping mercury electrode was known as polarography and the advances in our understanding of polarized interfaces was recognized by the Nobel Prize of Jaroslav Heyrovsky in 1959. Polarography was also pioneered by Masuzo Shikata to whom this lecture is dedicated.

David Grahame, in 1947, summarised the knowledge of the time in a famous review article\textsuperscript{5}), that had served as a reference for many textbooks.

During the second world war, the Russian school of electrochemistry\textsuperscript{6,7}) had questioned what would happen if the distribution of the charges on the electrode was not diffuse but discrete. This question of localised charges, and associated micro-potentials generated by these localised charges, was indeed difficult to treat. Nonetheless, D.C. Grahame showed that an interface composed of face-to-face localised charges would behave as a classical capacitor of capacitance equal to $\varepsilon S/d$ \textsuperscript{8}), where $\varepsilon$ is the permittivity, $S$ the surface area and $d$ the distance between the two charge monolayers.

Fig. 3. Potential distribution at an interface composed of face-to-face localised charges. Adapted from Ref. 8.

The main reason why it is important to understand potential distributions on electrodes or electro-active materials is that the potential is used in electrochemistry to vary the driving force of the charge transfer reactions, and is therefore at the center of all charge transfer theories.
Potential distribution at polarised liquid-liquid interfaces

Apart from solid/electrolyte interfaces, other types of interfaces can also be polarised, such the ITIES (Interface between Two Immiscible Electrolyte Solutions). As early as 1902, Nernst had shown that the interface between two immiscible solvents, e.g. water and phenol, could be polarised and the locus of charge transfer reactions such as ion transfer reactions, assisted-ion transfer reactions (including acid-base proton transfer reactions), and even dark or photo-induced electron transfer reactions between two redox couples located in the adjacent phases.

The structure of liquid-liquid interfaces has been received a lot of attention. In the early days, most of the information came from surface tension or capacitance measurements; then came surface sensitive spectroscopic techniques such as surface second harmonic generation, and finally molecular dynamics simulation provided snapshots and statistics of the interfacial structure.

Today, the view that the interface between two liquids is molecularly sharp has gained a wide acceptance.

When discussing the potential distribution at a polarised liquid-liquid interface, the early Verwey-Niessen model of two back-to-back diffuse layers had been widely used as it was apparently corroborated by surface tension and capacitance measurements. Recently, Gschwend et al. have questioned the validity of this model, and suggested that the localisation of the ionic charges at the interface were not always diffuse. Indeed, it was shown both by molecular dynamic simulation and surface second harmonic generation that the large organic ions tend to be present in the plane of the interface (as if specifically adsorbed...) and that their charge was counter-balanced by the presence of aqueous counter-ions moving around the slow moving large organic ions.

This model was termed the “Discrete Helmholtz model” as is illustrated in Figure 4, with the organic ions on one side and the aqueous counter-ions on the other side forming an ionic capacitor. This means that all the potential drop between the two adjacent phases occurs across the ionic capacitor and is not spread over two back-to-back diffuse layers.

Fig. 4. Discrete Helmholtz model at liquid-liquid interfaces. Adapted from Ref. 11.

This model provides some answers about the potential dependence of charge transfer reaction at ITIES. Indeed, if the potential drop was to be spread across two back-to-back diffuse layers, a key question was: How much of the applied potential difference contributes to the driving force of charge transfer reactions?

In its most simple form, the Discrete Helmholtz model gives the following answers. An ion transfer reaction can then be described as an ion crossing the interfacial ionic capacitor, meaning that all the potential difference acts as a driving force. An electron transfer (ET) reaction can then be described as a redox reaction between an organic electron donor (respectively an
acceptor) and an aqueous electron acceptor (respectively a donor) located on either side of the ionic capacitor. Again, in this case all the potential drop is acting on the electron transfer reaction thereby explaining the observed potential dependence of ET reactions at ITIES.

This model shows that the difference of sizes of the two ions makes the large organic ions behave as “anchoring” points generating a micro-potential where the potential gradient occurs not only perpendicular to the plane of the interface as shown in Fig. 4, but also in all directions around the anchoring point, even in the plane of the interface. This would mean that ET reactants could even be both located within the plane of the interface and yet be potential dependent.

All in all, the Discrete Helmholtz model does not solve all the issues of understanding potential dependent charge transfer reactions at liquid-liquid interfaces, but shines new light on possible mechanisms.

Ionosomes

Recently, Deng et al.14) have observed a new type of nanoemulsions where an aqueous phase is entrapped in an ionic bilayer comprising an inner layer of aqueous ions surrounded by an outer layer of organic counterions. These nanoemulsions are formed by transferring hydrophilic ions under potential control from water to oil. The co-transport of water brings the concentration of water in the oil phase above the saturation level thereby forming nanodroplets onto which the transferred hydrophilic ions adsorb and become covered by organic counter ions. These nanoemulsions illustrated in Fig. 5 have been termed “ionosomes” by analogy with the liposomes. They form spherical capacitors that can easily be modelled by the Discrete Helmholtz model.

These ionosomes carry a net charge of the same sign as those of the transferring ions forming the inner layer of the ionosomes, and upon reversing the potential, they can be electrophoretically driven back towards the aqueous phase. By a mechanism of “kiss and burst”, they disrupt upon contacting the interface and release the hydrophilic ions as recorded amperometrically as an ionic current spike.

This new form of ionic nanostructures opens new avenues and applications, for example in drug delivery.

Discrete Helmholtz model on non-metallic interfaces

The Discrete Helmholtz model may also apply to solid interfaces either conducting, e.g. metal oxides, or not conducting, such as silica.

If the surface is amphoteric, the surface charge density is pH dependent and as a result, the potential drop at such interfaces becomes also pH dependent. As a matter of fact, even today, the working mechanism of the glass pH electrode as not yet been fully elucidated, and the Discrete Helmholtz model can offer some explanations. As shown in Fig. 6, an ideal non porous amphoteric membrane, such as quartz, could in principle be
used to measure the pH of a solution with respect to a buffer on the other side of the membrane simply from the difference of the surface charge densities resulting in different potential drops across the two discrete Helmholtz layers.

Yet, if the surface charge, of say silica, is compensated by a layer of cations compensating the deprotonated silanol groups, this would raise some other questions regarding electro-osmotic phenomena, where it is usually assumed that the counter charge of the silica is distributed in a diffuse layer. When an electric field is applied parallel to the interface, the excess charge in the diffuse layer onset a hydrodynamic movement. The potential at the shear plane is called the Zeta potential, thus, if the Discrete Helmholtz model applies, then the shear plane would correspond to somewhere between the two face-to-face ionic layers.

Another interface, where the charges are localised, is the ion-exchange membrane /electrolyte interface. These membranes are extensively used, from electrodialysis to electrolysis and fuel cells, but the locus of the potential drop associated with the Donnan potential difference is rarely discussed. Again, according to the Discrete Helmholtz model depicted in Fig. 6, a simple layer of counter charges to the fixed charges at the surface of the membranes would be sufficient to account for the potential drop.

Finally, biomembranes are another topic where the Discrete Helmholtz model could be applied as the charge distribution at the surface of a biomembrane is not homogeneous, and further considering the high ionic strength in biological media, it is clear that any Gouy-Chapman diffuse layer would be very thin.

**Discrete Helmholtz model on electrocatalytic interfaces**

Most studies related to electrocatalysis are concerned with the presence of a catalyst layer on an electrode. Most of the electrocatalysts consist of nanomaterials in physical contact with the electrode, such that the Fermi level of the electrons on the electrode is equal to that on the nanoparticles. When two materials of different work functions are placed in contact, electrons must transfer to equilibrate the Fermi levels. This means that the surface charges are different on the bare electrode material compared to the nanomaterials yielding an inhomogeneous potential distribution at the electrode surface where again the Discrete Helmholtz model may come into play.

**Redox electrocatalysis**

Another important aspect of electrocatalysis is redox electrocatalysis where an electrically floating electron conductor facilitates the electron
transfer reactions between two redox couples in solution which would not otherwise react, for example when the number of electrons involved in the two half redox reactions are different or when the two reactants are not miscible in the same electrolytes\(^ {16}\). In our laboratory, we have used the concept of redox electrocatalysis to split water using an aqueous redox flow battery as shown in Fig.7. For example, if one side of an aqueous redox flow battery is concerned with the vanadium (II/III) couple in acidic media, the redox potential of the electrolyte can thermodynamically reduce protons to hydrogen. As the bulk reaction does not take place in solution, redox electrocatalysts with a surface appropriate for hydrogen evolution such as platinum or molybdenum carbide\(^ {17}\) can be used and hydrogen can be evolved under pressure in the catalytic reactor.

Similarly, if the positive side of the aqueous redox flow battery contains a redox couple able to oxidise water, e.g manganese (II/III)\(^ {18}\) or cerium (III/IV), then, in the presence of an electron conductor with a surface appropriate for oxygen evolution such as iridium or ruthenium oxide, oxygen can be evolved in another catalytic reactor producing protons.

This work clearly shows that “homogeneous redox electrocatalysis” in tank reactors offer an alternative route to hydrogen production, which remove the gas formation H\(_2\) and O\(_2\) away from the electrochemical cell.

**Batch water splitting**

One of the long-term objectives of our laboratory has been to develop new routes for what we call “batch water splitting”\(^ {19}\) using redox electrocatalysis at liquid-liquid interfaces. The concept is to photo-produce hydrogen with sunlight at a liquid-liquid with an organic electron donor that becomes oxidised with time as the aqueous solution becomes more basic, and to photo-produce oxygen at another liquid-liquid interface with an organic electron acceptor that becomes reduced with time as the second aqueous solution becomes more acidic. At night, the two aqueous phases are mixed to reset the pH and the two organic phases are mixed to react D\(^+\) and A\(^-\), resetting the concentrations of the sacrificial electron donors and acceptors. This electrodeless concept is illustrated in Fig. 8.
Fig. 8. Batch water splitting. Adapted from Ref. 19.

Hydrogen generation is the easy part of the scheme, as for example metalloccenes, such as decamethylferrocene, dissolved in the organic phase can even reduce aqueous protons in the dark at the interface. To reach higher potentials and to fully exploit the light energy, we have recently shown that we could use molecules such as decamethylruthenocene, which have a dark redox potential of 0.75V in dichloroethane versus an aqueous standard hydrogen electrode as shown below.

The bottleneck for designing an efficient batch water splitting process is oxygen evolution, but a recent work of Ragstar et al. using BiVO₄ at the water-butyronitrile interface is very promising as it was shown that oxygen could be photo-produced at the interface using the lipophilic [Co(bpy)₃]³⁺ ion as a redox mediator and where the adjacent aqueous phase acts as a proton pump.

The key advantage of the batch water splitting is to avoid the use of costly ion-exchanges membranes. The two photoelectrochemical reactions can take place in transparent polymer tubes directly placed on the ground.

Molecular electrocatalysts for water splitting.

In a recent publication, we have shown that we could use the concept of redox electrocatalysis for photo-oxidising water, using tetrathiafulvalene cations TTF⁺, as a sensitiser and TTF as the redox mediator. In this work, the water oxidation takes place in a water-acetonitrile mixture to dissolve the organic salts and to provide excess water for the reactions. At the time, it was considered that the platinum microparticles could provide the electrons to reduce the photo-excited TTF⁺ on the one hand and to oxidise water on the surface of the platinum on the other hand.

In fact, we have shown that TTF and TTF⁺ formed molecular assemblies such as nanorods. Indeed, water oxidation to oxygen requires four electrons that can only be provided if these ions are pre-assembled to be able to form the oxygen-oxygen bond. So, it was not clear if the oxygen production observed took place on the platinum or on organic molecular assemblies.

The scheme of the overall reaction is show in Fig.10.
became limited by the protonation of the TTF molecules as water oxidation generates protons. Protonated TTF can in turn be photo-sensitised to carry out hydrogen evolution\(^{24}\).

**Conclusion**

All in all, we have shown that it is essential to apprehend the most fundamental aspects of potential distribution at polarized interfaces to develop new methods for energy conversion and storage, so much needed for the energy transition. In particular, it will be important in the future to better understand potential distribution not only on model electrode systems, but also on industrially relevant electrodes.

After a century of chemical industry based on the use of fossil resources, the coming years will see the development of new electrochemical processes as renewable electricity will become a cheap commodity.

If most industrial electrochemical processes so far rely on the use of ion-exchange membranes and solid planar electrodes, it is worth developing new processes based on soft interfaces and “homogeneous redox electrocatalysis” to invent new systems mimicking natural photosynthesis.

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