



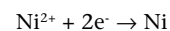
Physical and Analytical Electrochemistry: The Fundamental Core of Electrochemistry

by Tom Zawodzinski, Shelley Minteer, and Gessie Brisard

The common event for all electrochemical processes is that of electron transfer between chemical species; or between an electrode and a chemical species situated in the vicinity of the electrode, usually a pure metal or an alloy. The location where the electron transfer reactions take place is of fundamental importance in electrochemistry because it regulates the behavior of most electrochemical systems. It is at this interface of the electrode and solution that the electric field present has a determinant role in the charge distribution within reactants as well as in the position and orientation of the reactant to form the desired products. Figure 1 schematizes a heterogeneous interface. **Physical Electrochemistry** deals with the thermodynamics and kinetics (rates and mechanisms) of those processes. Many research topics are concerned with the details of reactant and interfacial structure, and how they affect the kinetic parameters for electron transfer reactions. **Analytical Electrochemistry** is the application of electrochemical processes to measure the quantity of a species of interest. In this article, we describe the types of processes and their applications in analytical measurements and in electrochemical systems and devices. In analytical measurements, we try to control or isolate the contributing processes to facilitate the determination of the system's composition; while for systems and devices the objective is the optimization of the processes to enhance, for example, the electrical efficiency or temporal response of the system. Some examples of electrochemical systems and devices that play an important role in many areas of sciences and technology include electro-organic synthesis, batteries and fuel cells, photoelectrochemical cells, electroplating cells, electrodialysis, corrosion systems, sensors, and measuring devices in many areas of medicine and biology.

Electrochemical Systems

The simplest and traditional electrochemical process occurring at the boundary between an electronically conducting phase (the electrode) and an ionically conducting phase (the electrolyte solution), is the heterogeneous electro-transfer step between the electrode and the electroactive species of interest present in the solution. An example is the plating of nickel.



The interface is where the action occurs but connected to that central event are various processes that can occur in parallel or series. Figure 2 demonstrates a more complex interface; it represents a molecular scale snapshot of an interface that exists in a fuel cell with a solid polymer (capable of conducting H^{+}) as an electrolyte.

However, there is more to an electrochemical system than a single interface. An entire circuit must be made for measurable current to flow. This circuit consists of the electrochemical cell plus external wiring and circuitry (power sources, measuring devices, etc). The cell consists of (at least) two electrodes separated by (at least) one electrolyte solution. Figure 3 is a schematic of a simple circuit. Each electrode has an interface with a solution. Electrons flow in the external circuit but the solution is essentially an electrical insulator. For current to flow, a chemical to electrical transduction event must occur at the interface. Electron transfer between the electrode and solution species, called a faradaic process, is the means by which this transduction occurs. Because the circuit is completed via the faradaic process, a current can flow through the cell. To support such a current, the solution must be, to some extent, an ionic conductor.

Primary variables associated with the electrochemical process are the potential of the electrode, which is a measure of the electron *energy* at the (metal) electrode surface, and the current, which is a measure of the *rate* of the process, sometimes given as a current density, current per unit electrode area. Together, these variables define the flux (material per unit time per unit area) as a function of the electron energy. Note that we are strict throughout this article in referring to the potential of a single electrode and the voltage (or potential difference) between two electrodes. Even that nuance has nuances!

We mentioned that at least two electrodes are used. In most systems for device applications, two electrodes are the norm but in analytical systems, however, three electrodes are used. The reason for the various electrodes

is easily pictured if we consider voltage drops across the electrochemical cell. While current is flowing between electrodes, there is a voltage drop at each electrode/solution interface and across the electrolyte (typically called solution IR loss due to its Ohmic properties). Because the goal of an analytical system is to measure the amount of some species or, perhaps, the rate of a process at a known potential, we must focus on one electrode in the cell, called the working electrode, at which this species undergoes a redox reaction to give us our analytical change in current or voltage. In careful analysis, it is generally important to also know the potential of the working electrode. This can be known only relative to that of another electrode, which is referred to as a reference electrode. If a two-electrode cell is used, the second electrode is called an auxiliary electrode. The current flows between the two electrodes and the auxiliary electrode functions both to carry the current (via a redox process) and as a reference electrode. Thus the potential difference between the two electrodes includes both the difference in the redox potentials at the respective interfaces and the IR loss. The latter is not necessarily well known, because the solution resistance can be a complicated, potential and frequency-dependent quantity. To get around this, the two functions are often separated. A third electrode, a reference electrode with a well-defined redox potential, is positioned close to the working electrode (to minimize IR loss) and electrode two is now referred to as a counter electrode.

Processes

Now let us consider what is happening in the cell. It is crucial to keep in mind that all these processes occur simultaneously. Fortunately, we can often think about them one at a time, known as the superposition principle. We can summarize what must happen from the viewpoint of the redox active species. In simplest terms, it must make it to the electrode, react somehow, and then leave the electrode. We are usually concerned with the time scale or rate of these processes, the energetic driving forces for reactions to occur, and the detailed mechanisms of how they occur.

Making it to and from the Electrode:

Mass Transport. To get to the vicinity of the electrode, there are three transport mechanisms to consider:

1. Diffusion is transport due to random thermal motions. This is a random process on the molecular length scale that acquires directionality at macroscopic length scales because of concentration differences (gradients)

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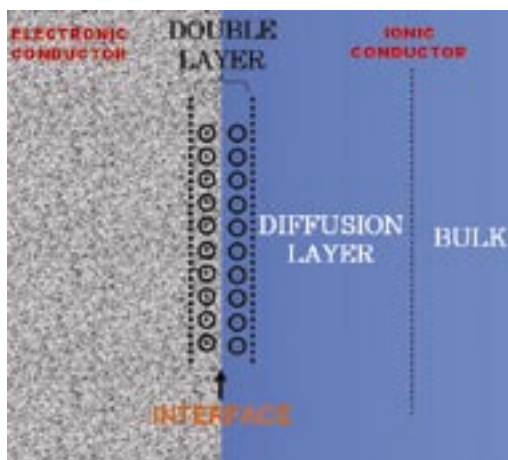


Fig. 1. Schematic of the structure of a heterogeneous electrochemical interface.

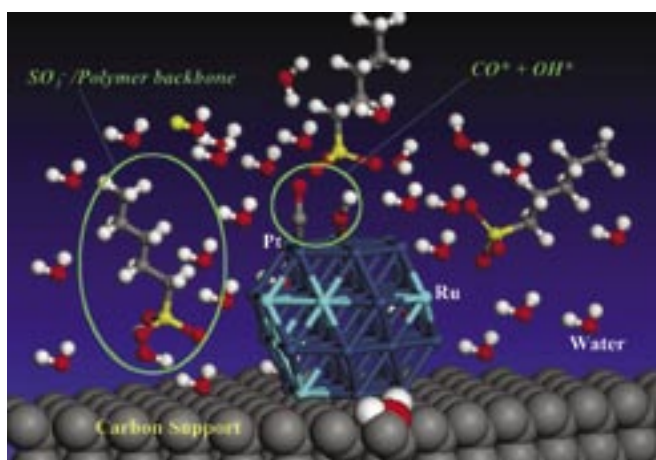


Fig. 2. An electrochemical interface of a fuel cell electrode. What is shown is a molecular level picture of a Pt/Ru alloy nanoparticle on a carbon support, the electrode, surrounded by water molecules and polymer electrolyte fragments (labeled $\text{SO}_3^-/\text{polymer backbone}$) with adsorbed CO and OH species. (Figure courtesy of Professor Matt Neurock, University of Virginia.)

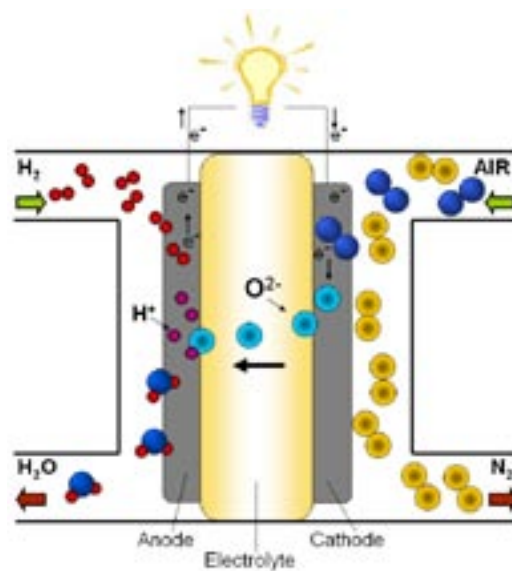


Fig. 3. A complete circuit made of a two-electrode electrochemical cell representing a solid oxide fuel cell in which the electrolyte is an oxygen ion conductor. The reactions are the oxidation of hydrogen at the anode to form H^+ and reduction of dioxygen at the cathode.

Physical and Analytical...

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in the cell. There is a nuance here: the actual gradient driving diffusion in the macroscopic sense is that of the chemical potential or activity. For dilute solutions, concentration is adequate substitute and keeps the math simple. We can use Fick's laws of diffusion to analyze the process. For concentrated solutions, more sophisticated treatments are needed.

2. Convection is transport due to the concerted bulk flow of the solution. In this process, the redox species of interest is carried along with the flow of solution. In many large-scale electrochemical processes, the solution can also be pumped through the cell. A mathematical description of this process via fluid mechanics can be complex, but sometimes the geometry is rigged to simplify this description.

3. Migration is transport in response to a potential gradient and is strictly relevant to charged species.

Regarding transport, the fastest mode wins, and will dominate the observed behavior. Convection and migration are generally faster modes of transport than diffusion, in part due to their intrinsically directional nature. When we want to be as quick as possible, such as producing a product in bulk electrolysis or trying to maximize the performance of a battery or fuel cell, this is fine. If we are trying to analyze a process, we want control over the mass transport, often focusing on diffusion, the slowest mode. To minimize convection, we work in an unstirred system, minimize pressure differentials, and cut vibration. If we want to minimize migration, we use an uncharged species (we may not have any choice in this!) or we can swamp out the effect for the ion of interest by putting in many other ions to carry the current. The latter approach is called using a supporting electrolyte.

How do we characterize the relative rates of these processes? Typically, we consider the resistance to the process or its inverse. For diffusion, the rate is determined by the size of the diffusing species, the solution viscosity, and so on. That information is summarized in a diffusion coefficient, D , which has units of $(\text{length})^2/\text{time}$ typically on the order of $10^{-5} \text{ cm}^2/\text{s}$ for a species in aqueous solution. For convection, the flow rate and concentration determine the net rate of arrival at the electrode. For migration, we consider two things analogous to flow rate and concentration, namely, the electrolyte conductivity, the inverse of the resistance to migration, and the transport number of the species of

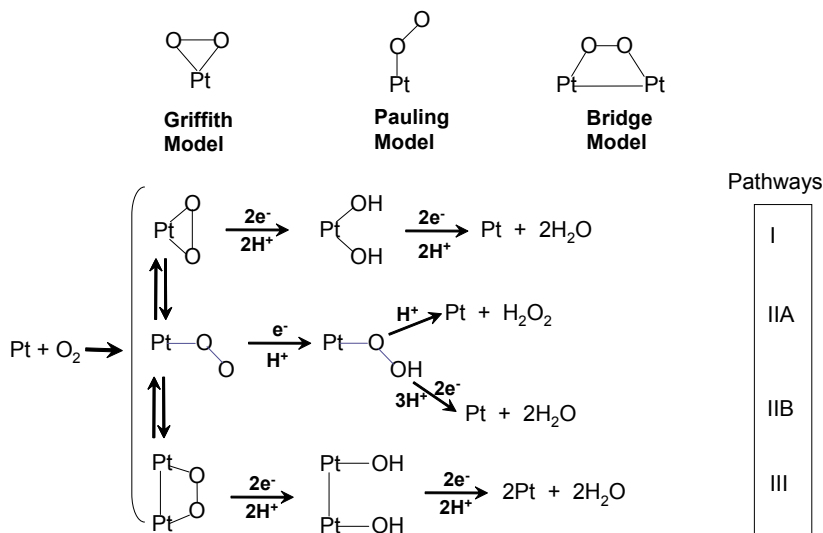


Fig. 4. Postulated O_2 reduction pathways.

interest, the fraction of charge carried by that species.

Applications: Electrocatalysis

Considering some complex redox processes may serve to solidify the discussion above. In electrocatalysis, the electrode functions as a catalyst, an unchanged reagent that facilitates a chemical change. We consider briefly two processes involved in fuel cell reactions, the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR), both occurring on Pt electrodes and separated by an electrolyte. The Pt on the oxidation side is the anode and the Pt on the reduction side is the cathode.

In the HOR, a hydrogen molecule H_2 is oxidized in a series of steps. A dissociative chemisorption step involves the simultaneous dissociation and adsorption of the H_2 to form two Pt-H moieties. The H then is oxidized to form H^+ and is released from the electrode into the electrolyte. This is a rapid reaction on Pt. The H-H bond strength is not particularly large thus Pt-H formation is facile. Each hydrogen atom releases a single electron.

The ORR is a much more complicated reaction sequence (Fig. 4). First the reaction involves transfer of four electrons and four protons to give water. Again, there is an initial adsorption step followed by a sequence of e^- and H^+ (present in the electrolyte) transfers. During this sequence, various intermediates are formed. The O-O bond is itself strong. At the cathode, lots of competing side pathways are in progress. The ORR is an enormously important reaction from a practical viewpoint because it is a good oxidant that is essentially free.

One final note: all electrocatalytic processes are strongly influenced by the nature of the catalytic surface itself. This nature includes both the nominal composition (e.g., Pt, Au, or Ni) and the actual composition (oxide layers and so on). As indicated above, the details of mechanisms involve various interactions between molecules and surfaces and the strength or weakness of these interactions depends on the chemistry between the true surface and the redox molecule. The spacing of atoms on the electrode surface, which is different for different metals, influences the adsorption mode of the reactive molecule. For example, O_2 can adsorb in either an end-on or a bridging mode.

Applications: Electroanalysis

In our illustration of the various processes discussed above, we consider some of the special requirements and approaches of electroanalytical measurements. Generally, in electroanalysis we are trying to achieve a well-defined situation enabling a quantitative relationship to be established between a measurable electrical quantity (current, charge, or potential) and the concentration or amount of material (analyte) present in a sample. Thus, we often control current or potential on the analytically active (working) electrode. This control is usually achieved with an instrument called a potentiostat. In a typical case, we scan or step the control variable and measure the response of the dependent variable. As noted above, we also must control the mass transport behavior in our cell and ensure that our measured or controlled potential is determined accurately, entailing a three-electrode cell.

Some typical methods entailed include:

Cyclic voltammetry: the working electrode potential is scanned linearly with time and cyclicly throughout a potential window of interest; the current response is measured, typically plotted vs. potential.

Potential step methods: the working electrode potential is stepped from a region in which nothing happens to a potential at which the redox reaction occurs; the current is measured vs. time (chronoamperometry). This approach also forms the basis for the family of analytical methods called pulse voltammetry, in which a combination of multiple steps of varying magnitude is applied and the current sampled in time to construct a current-voltage response.

Rotating disk method: a slow cyclic voltammetric scan is imposed on an electrode that is rotated to create a well-defined convective mass transport pattern, resulting in a steady-state voltammetric response particularly amenable to analysis.

Potentiometry: all the above controlled-potential methods have analogues in which current is controlled and potential is measured. Also, the thermodynamically determined potential can be measured at open circuit (*i.e.*, with no current flow) to yield a measure of concentration.

These brief descriptions are but a tiny fraction of the many methods available in the electrochemist's toolbox. We have included at the end of this article a list of classical readings, excellent available texts, and specialist monographs on electrochemistry, that cover in more detail the theory and applications of physical and analytical electrochemistry.

Examples of Research Problems of Interest to this Community

To provide a flavor of the sort of research problems of current interest to this Division, the following topics were presented as symposia at recent ECS meetings. To this day, the topic of "Molecular Structure Effects in Heterogeneous Electron Transfer Kinetics" continues to be a fundamental issue; it involves the interfacial structure and aspects of interest include the distribution of charge in the double layer, the effects of specifically adsorbed ions and molecules, and self-assembled monolayers. The "Electrochemistry of Novel Materials" is another popular symposium organized by the PAED. Materials are the core of new electrochemical systems and the search for more catalytically active or sensitive electrodes constitutes an

important activity for members of this Division. The researchers are interested in the electrochemical properties, preparation, characterization, responses, and applications of novel materials. Some examples are nanoparticles and nanostructured materials, electrocatalysts (metallic, nonmetallic, or modified materials), magnets, ion and proton conductors, and glasses and amorphous media. Materials for analytical and electronic devices such as ceramic, silicon continue to be improved. In the past decade, the field of energy and the environment such as fuel cells, batteries and energy generation and storage has concentrated much of the efforts of physical and analytical electrochemists. A symposium on "Three-Dimensional Micro- and Nanoscale Battery Architectures" focuses on a defining characteristic of 3D batteries: transport between electrodes remains one-dimensional (or nearly so) at the microscopic level, while the electrodes are configured in complex geometries (*i.e.*, nonplanar) to increase the energy density of the cell within the footprint area. A 3D matrix of electrodes (in a periodic array or a periodic ensemble) is thus required to meet both the requirements of short transport lengths and large energy capacity. Improvements in energy per unit area and high-rate discharge capabilities are two of the benefits that may be realized for these 3D cells. In the symposium on "Environmental Electrochemistry," electrochemistry is used both to detect and quantify the pollutants and to directly remediate polluted environments. In these areas electrochemistry offers the advantages of automation, detectability, selectivity, inherent cleanliness, and in many cases, cost effectiveness.

Analytical electrochemistry also remains a fundamental part of the research such as "Electrochemical Detection of Biomolecules" and "Electrophoresis and Microfluidics." This year a special symposium is being organized to honor the memory of Professor Robert A. Osteryoung. Professor Osteryoung's passing in 2004 was a tremendous loss to the field of physical electrochemistry. For over half a century Professor Robert A. Osteryoung sought to extend the frontiers of electrochemistry with contributions spanning the gamut from technique development to instrument design and automation.

Today's state of the art is to focus on the interface between the fields of chemistry and physics. A good example is the symposium on "Electrochemistry and Spectroscopy." (Many spectroscopists have become addicted to electrochemistry!) Examples

of research problems include (i) fundamental studies of electrocatalysis reaction pathways for oxidation of fuels using electrochemistry combined with reflectance IR spectroscopy or second harmonic generation spectroscopy to detect the presence and nature of adsorbed intermediates, (ii) electrochemical NMR for the study of the nature of adsorbates on electrodes; (iii) electrochemical and ellipsometry studies of the formation of oxide layers on metal electrodes; and (iv) determination of ion and solvent transport rates using conductivity measurements along with diffusion measurements employing NMR spectroscopy or specially designed electrochemical cells. ■

Suggested Reading

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