

ELECTROCHEMISTRY

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Keywords: Electrode, Electrolysis, Galvanic Cell, Fuel Cell, Double Layer, Nernst Equation, Butler-Volmer equation, Battery.

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Summary

The nature of electrochemical processes is introduced in this chapter starting from the most basic concepts. After an historical overview, two key concepts are introduced. First, when a metal is immersed into an electrolyte solution a potential difference is established between the two phases, that, under equilibrium conditions is characteristic of the chemical nature and composition of the metal and the solution. Although this potential difference cannot be measured, it is a key concept in electrochemistry. Second, when the potential is forced outside this equilibrium value, a net current flows through the interface. A brief description is given of the relations between equilibrium potential and composition and between potential and current. A different topic is the microscopic description of the metal solution interface, of great value to understand the mechanism of electron transfer between the two phases. The chapter finishes with a brief description of the most important applications of electrochemistry in everyday life.

1. Introduction

In a broad sense, the word electrochemistry would refer to the science that studies those chemical conversions in which electrically charged species are implicated. Given the electrical nature of matter, this definition would include almost every chemical reaction, since in almost every reaction there will be a transfer of electrons among the atoms of the participating species, during the splitting and formation of chemical bonds. However, the term electrochemistry is usually employed in reference to those reactions in which charged species can be identified as real components in the reaction medium. A general definition of electrochemistry would be: Electrochemistry is the science that studies the properties and chemical transformations of/within ionic conductors (most commonly a solution of a salt) and at the interface between an ionic conductor and an

electronic conductor (most commonly a metal) or semiconductor. In this very definition, two broad and well differentiated areas can be distinguished, depending on the number of phases present in the system. First, the study of ionic conductors constitutes the subject of one part of electrochemistry called *ionics*. In this case, all charged species are located in a single phase. Then, although electrostatic interactions between ions determine in great extent the properties of the phase, there are not macroscopic potential differences in it. This part of electrochemistry includes the study of electrolytic solutions, i.e., the solutions formed after adding a salt to a polar solvent, aqueous solution being with difference the most studied. The parameters that determine the thermodynamic properties of the solution would constitute one part of ionics. This means understanding chemical reaction in solution, vapor pressure, boiling and freezing temperature, etc. The movements of ions in the solution, driven by concentration gradients (diffusion) or by the passage of current, constitute a second part of this area of electrochemistry. Figure 1 summarizes the division of Electrochemistry in different areas.

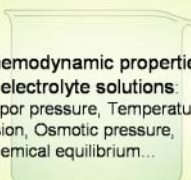
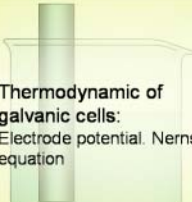

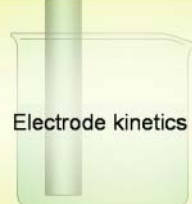
	1 phase	2 phases
Equilibrium	 <p>Thermodynamic properties of electrolyte solutions: Vapor pressure, Temperature of fusion, Osmotic pressure, Chemical equilibrium...</p>	 <p>Thermodynamic of galvanic cells: Electrode potential, Nernst equation</p>
Change	 <p>Transport properties in electrolyte solutions: Diffusion and conduction of electricity.</p>	 <p>Electrode kinetics</p>

Figure 1. Different areas in Electrochemical Science

When charged species can circulate between phases (for instance, a metal and an electrolytic solution), new concepts become relevant, such as the electric potential of the phase and the potential difference between phases. This is the subject of the part of electrochemistry called *electrodics*. This includes the study of the thermodynamic properties of the interphase and the relation between the different parameters (concentrations, potential difference, temperature, pressure...) that govern the rate of electron transfer through the interface. [*Here, the term interface refers to the bidimensional surface that separates the metal and the solution; conversely, interphase is the three dimensional region located between the bulk metal and the bulk of the solution characterized by particular values of the state variable that change progressively from the values in one phase to the values in the other phase*]. This is by far the most active part of electrochemistry in today's research and includes the study of the interconversion of electrical and chemical energy. This conversion can be in both

directions. The generation of electricity from the energy stored in chemical bonds leads to the concept of batteries and galvanic cells. The driving of chemical reactions by the use of electrical energy leads to the concept of electrosynthesis. In the first case, electrons can be considered a product of the chemical reaction, in the second they are one of the reactants. Both processes have a tremendous impact in our daily life. We don't need to say how important batteries have become in our world, full of portable gadgets, but it is necessary to stress that they are expected to become a fundamental part of our life if the plans to reduce CO₂ emissions follow the directions envisioned today, through the implementation of fuel cell as new key elements in the generation of both stationary and mobile electricity. Fuel cells constitute one of the most active fields of research in electrochemistry nowadays. Electrosynthesis plays also a very important role in today's society, and processes like chlorine and aluminum synthesis stand out with productions of megatons every year.

1.1. A Historical Perspective

An iconic experiment in the history of electrochemistry took place in Bologna, Italy, in 1791, when Luigi Galvani was able to produce electricity by inserting metal pieces into frogs' legs. This experiment has often been regarded as the birth of "modern electrochemistry" and in honor to Galvani, the term galvanic cell is widely used today. Nine years later, in 1800, Alessandro Volta described his famous pile, formed by a series of discs of two different metals, such as silver and zinc, separated by a paper wet with brine. From this date, the development of electrochemistry ran parallel to that of the science of electromagnetism, with important contributions also to the development of chemistry. In the years that followed the announcement of Volta's pile, different scientists suggested and constructed different electrochemical cells. Even before Volta's discovery was published, in June 1800, Nicholson and Carlisle discovered the capacity of electricity to split water into O₂ and H₂, although, at the beginning, the phenomenon was not completely understood. In 1806, Theodor Christian Johann Dietrich von Grotthus proposed his famous mechanism about the conduction of electricity through ionic solutions. At that time, it was not known that salt dissociate in water solution and therefore, it was very surprising that different gases would be evolved on different electrodes. If water molecules were split on the electrode, then both gases would be evolved on both electrodes. Von Grotthus imagined that the passage of electricity through the solution would polarize the water molecules that he imagined composed of positive and negative ends, forming chains with each positive end of a molecule associated with the negative end of an adjacent molecule. At the end of the chain there would be the electrodes. At the negative electrode it would take place the neutralization of the positive end of the chain, while at the positive electrode, the negative part of the water molecule would be neutralized. Then, each molecule would interchange partners with the adjacent water molecules, resulting in a passage of charge from one electrode to the other without the molecules really traveling through the solution, and every ion always attached with a corresponding counterion. We know nowadays that this vision is not correct since salts, when dissolved in water, split into ions and the ions are the responsible for the passage of electricity through solutions. Still, a mechanism very similar to that proposed by von Grotthus is believed to take place for the movement of protons and hydroxyls through solutions and this mechanism is called today Grotthus mechanism.

Only 7 years after the discovery of the electric pile and the electrolysis, Sir Humphry Davy was able to use electricity to isolate a number of chemical elements, such as potassium, sodium and calcium. Volta's discovery of the chemical generation of electricity gave the scientists of the period a continuous source of electricity. The different sources of static electricity available until this date were only able to create transients currents and therefore, it was difficult to use them to progress in the advancement of the science of electromagnetism. This is why the discovery of the galvanic cell is so intimately linked to the progress in the understanding of electromagnetic phenomena. In 1820, Hans Christian Oersted found that a compass needle is subjected to a force when is near a cable connected to the poles of a battery. This result was described later the same year in a detailed mathematical manner by the French scientist André Marie Ampère. His complete analysis was published in 1823.

Another fundamental name in the history of electrochemistry is Michael Faraday. In the years that followed Oersted discovery, Faraday performed different experiments in this subject. In 1831 he made one of his most famous discoveries, the electromagnetic induction. In the field of electrochemistry, Faradays is famous for his laws of electrolysis. Faradays studies on electrolysis led him to introduce several terms which have today ubiquitous usage in chemistry: electrode, electrolysis and electrolyte are terms introduced by Faraday, after suggestion of his friend and personal physician Whitlock Nicholl. Also, the terms anode, cathode, anion, cation and ion were suggested to Faraday by William Whewell in 1834. This same year, Faradays suggested, based on his novel understanding of the phenomenon of electrolysis, his laws of electrolysis. The first law states that the amount of material deposited or evolved during electrolysis is proportional to the amount of electricity that passes through the solution. So far, an idea based on the concept of central forces was generally accepted to understand the process of electrolysis. If this were true, the amount of deposited material would depend on the electric potential applied to the electrodes or to the distance between them. Faraday demonstrated that this was not true. The second law of electrolysis relates the mass of deposited material with the equivalent weight of the substance being deposited. Although these laws have been shown correct and are widely used and taught nowadays, Faraday reached them from erroneous concepts. In his view, the effect of electricity was to produce the dissociation of the components of the solution that he imagined as electrically neutral in a similar way to Grotthus ideas.

A lot of interest appeared in the scientific community of that time about these issues. A number of different cells were proposed in the decades that followed Volta's discovery. In 1836, John Frederick Daniell showed his famous cell, consisting of Zinc anode in sulfuric acid solution and a copper cathode in copper sulfate solution. This cell is used in most electrochemistry textbooks to introduce the basic concepts associated with galvanic cells. Another cell worth mentioning is that of Sir William Robert Grove, who presented in 1838 a cell consisting of zinc cathode and an anode formed by platinum in nitric acid, both compartments separated by a porous material. This and Daniell cell were widely used in the early days of telegraph communication. But Grove is mostly remembered today as the father of fuel cells. In 1939 he published what has been considered the first fuel cell in history. It consisted of four cells formed by platinum electrodes in different vessels containing hydrogen and oxygen gases and a sulfuric acid solution. Figure 2 shows a diagram of this cell. The electricity generated by this cell

was used to produce water electrolysis. Careful measurements showed the relation between the gases consumed and those produced during the electrolysis. Little importance was given to this discovery at the time, and it was not until one decade later that this technology was rediscovered. In fact, fuel cells were chosen by the NASA to produce the electricity necessary for the missions Gemini and Apollo and they are considered nowadays one of the most promising technologies capable to alleviate the energetic crisis that we are living at present.

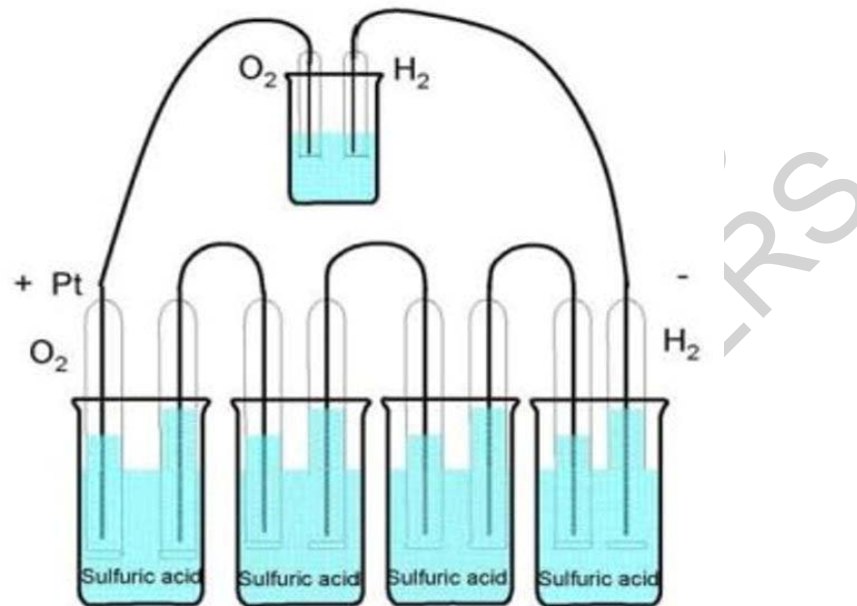


Figure 2. Schematic representation of the first Fuel Cell by Sir William R Grove in 1839.

The next step towards the understanding of the mechanism of conduction of electricity through electrolyte solutions was given by Rudolph Julius Emmanuel Clausius, who found that Ohm's law, which relates the current circulating and the potential difference at the extremes of an electronic (metallic) conductor is also obeyed by electrolyte solutions. This contrasted with the ideas at the moment. If according to Faradays view, the effect of the electric current is to cause the dissociation of neutral molecules, a threshold value of potential would be necessary to start the current. Clausius suggested that a small amount of ions are always present in the solution. These ions would be responsible for the conduction of electricity. Other significant experiments in this regard were done by Friedrich Wilhelm Georg Kohlrausch, who discovered in 1874 the law of independent migration of ions that shows that the conductivity of the salt can be understood as the contribution from the ions that constitute it and that each ion, in the limit of infinite dilution, contributes to the conductivity of the solution the same amount regardless of the salt in which it was present. In 1889, Svante August Arrhenius proposed his theory of electrolytic dissociation to explain the deviation observed by van't Hoff in the vapor pressure of electrolyte solutions.

The thermodynamic of galvanic cells was developed during the second half of the

nineteenth century, especially through the contribution of Walter Nernst. The kinetic study of electrode processes (the relation of the rate of electrochemical reaction and the electrode potential) was delayed to the beginning of the twentieth century. One of the most important contributors to this subject was Julius Tafel, who proposed the exponential relation between the current and the electrode potential, an equation that is now known as Tafel equation.

1.2. An Overview of Applications

Electrochemistry is present in a wide range of application in our daily life. One of the most obvious applications is that of batteries. As outline above, batteries constituted the first stable generators of electricity in the nineteenth century. Later with the invention of the dynamo and the wide expansion of grid supply of electricity, the use of batteries has been relegated to applications where mobility is an issue. This is by no means a small application and it is becoming more and more important with the expansion of electronic gadgets, such as laptops, mobile phones, mp3 players, etc. Batteries have been present almost from the beginning in cars to start ignition motors and are also useful as electricity supply in remote location where grid power is not available, may be associated to other generators that rely on non constant energy sources such as wind or solar energy. Batteries are used in electric cars although strong limitation is derived from the long times usually needed to recharge them. Fuel cells can be considered as the next generation of batteries in which the main difference is that instead of recharging by regeneration of chemicals through the passage of current, the chemicals are directly added as new fuel that is continuously converted to electricity. Fuel cells are a reality nowadays. The first models with real applicability were developed during the Second World War and they were already used in the aerospace project that culminated with the landing of the man on the moon. Nowadays, several models are already commercialized both for stationary and mobile application although they are still seen as exotic and expensive devices.

The second important application implies the opposite process of batteries. This is the use of electricity to generate new chemical products. In this case electricity can be viewed as an additional reactant added to the reaction mixture. This process is called electrosynthesis and has several advantages in respect to a standard chemical process. Electricity is relatively cheap in comparison with other chemical substances that can be used as reactants. The number of by-products is usually smaller. And the control of the process can be achieved with greater simplicity since potential and current can nowadays be easily regulated with electronic instrumentation. Reaction can be easily stopped by just unplugging the reactor. Industrial processes of electrosynthesis are chlorine and alkali synthesis, aluminum synthesis and the synthesis of adiponitrile (used in the synthesis of nylon).

Purification of metals can also be performed by electrolysis. The raw metal can be dissolved in the anode of the cell and redeposited at the cathode. Because the deposition process depends strongly on the potential of the cathode electrode, by selecting this carefully, a selective deposition of the desired metal can be achieved. Electroplating is another typical application of electrochemistry. A thin layer of a metal is deposited with decorative (gold, silver or chromium) or protective purposes (anodized aluminum).

Electrochemistry finds also a wide range of application in analysis. The instrumental measurement of pH is based on the measure of the electrode potential in a galvanic cell where one of the electrodes is sensitive to pH. The same principle allows measuring other ions and today electrodes sensitive to different ions are widely commercialized. Other gases, such as oxygen or hydrogen can also be potentiometrically determined. The use of biomodified electrodes, for instance after the attachment of enzyme or immune-receptors on the electrode surface, opens the possibility for the fabrication of extremely sensitive and selective biosensors.

Another field where electrochemical science finds relevance is the study of corrosion processes. Corrosion is due to the dissolution of a metal due to the undesired formation of local galvanic cells on the surface of the metal. Most common cathodic reaction is the atmospheric oxygen reduction to water. Another possibility would be hydrogen evolution during the corrosion of a non-noble metal in acidic solution (e.g., zinc corrodes in acid solution). The purpose of electrochemistry in this field is to understand the mechanism of corrosion and to devise methods to avoid it. Cathodic protection with a sacrificing anode is the common method used to protect the cask of every ship that navigates the seas in present days.

Electrochemistry has also something to add to the sustainable development of our society. Besides its contribution through fuel cells, and the more environmentally friendly electrosynthesis processes described above, other examples are the treatment of residual water, elimination of organic material by electrooxidation, recovery of heavy metals by electrodeposition, electrocoagulation, electrodialysis. Lastly, it is worth mentioning a striking idea that is receiving a lot of research today. This is the use of microbial electrodes to obtain energy from the degradation of waste waters.

2. Thermodynamic Treatment of Charged Phases

The science of Thermodynamics studies the relation between the variables that define the state of a system, such as temperature, pressure, concentrations, etc and its properties. One important issue is the equilibrium distribution of the components of the system through all its parts. If only one phase is present, all variables will be homogenous at equilibrium. If there is more than one phase in the system, the variables will vary from one phase to the other. At thermal and mechanical equilibrium, temperature and pressure will be constant throughout the system. However, concentration may change from one phase to the other.

When charged species are involved, the electrical potential becomes a new relevant magnitude to understand the thermodynamic properties of a system. If there is only one phase, the electrode potential will be homogenous in equilibrium and all charged species will sense the same potential. Then the electric potential of the phase is irrelevant. In other words, because electric potential is a relative magnitude that needs always to be referred to a reference point, the reference can be taken such as the electric potential of the phase is zero. A different situation arises if more than one phase is present in the system and charged species can flow through the phases. In this case, because small charge differences will arise on the surface of the phases, the electric potential of each phase will in general be different. Then, ions will move between

phases driven by two forces, chemical and electrical in nature.

One example of this situation is the potential difference that arises when two metallic conductors (two different metals) are brought into contact. Before the contact, each metal is electrically neutral and composed of a cloud of electrons moving freely through a net of positively charged atomic nucleus. Because of the Fermi exclusion principle, the electron will adopt a distribution of energies, filling the different energy levels in the metal. The energy of the last filled level (strictly speaking at zero Kelvin temperature) is called the Fermi level of the metal. This situation is depicted in Figure 3, where the striped bands represent the distribution of electrons through the different energy levels in the metal. In this figure Φ represents the work function of the metal, this is, the minimum energy required to extract an electron from the Fermi level and take it into the vacuum. Because the two metals involved in this imaginary experiment are of different chemical nature they will have different Fermi levels. When the metals are brought into contact, the electrons situated at higher energy levels will “fall” to the lower empty energy levels of the other metal. This will create a deficit of electrons on one metal (M1) and an excess of electrons on the other metal (M2), and a potential difference between the two metals will be created. The existence of an electrical potential shifting the energy level of the electrons has been denoted in Figure 3 by the magnitude Ψ . This is the outer potential of the metal, which means the electrical potential just outside the metal phase. This potential will oppose to the transfer of electrons between the two metals and soon a new equilibrium situation will be achieved and the flow of electrons will cease. At that moment, the energy of electrons (with respect to the vacuum level) will be the same on both metals and they will have no reason to travel from one metal to the other. In fact, the amount of electrons that are necessary to create a macroscopic measurable potential difference is so small that in general the metals in this imaginary experiment can be considered electrically neutral. A similar situation takes place when a piece of metal is introduced in an ionic solution, as depicted in Figure 4. At the beginning there will be no equilibrium between the two phases and different components will travel through the interphase. To simplify things, let's assume that the solution contains the ions M^+ resulting from the ionization of the metal. This is the case when we immerse a zinc piece into a $ZnSO_4$ solution or a copper piece into a $CuSO_4$ solution. Then, the obvious process that will take place will be the equilibration of M^+ in the solution with those in the metal. Either if M^+ travels from the solution to the metal, creating an excess of positive charge in the metal (as depicted in the figure) or if it travels from the metal to the solution, creating the excess of positive charge in the solution, a potential difference between the two phases will appear as a consequence of the ion transfer. As in the previous example, the potential difference will oppose to the transfer of ions from one phase to the other and this transfer will cease soon. At the end, a new equilibrium situation is achieved characterized by a potential difference between the phases.

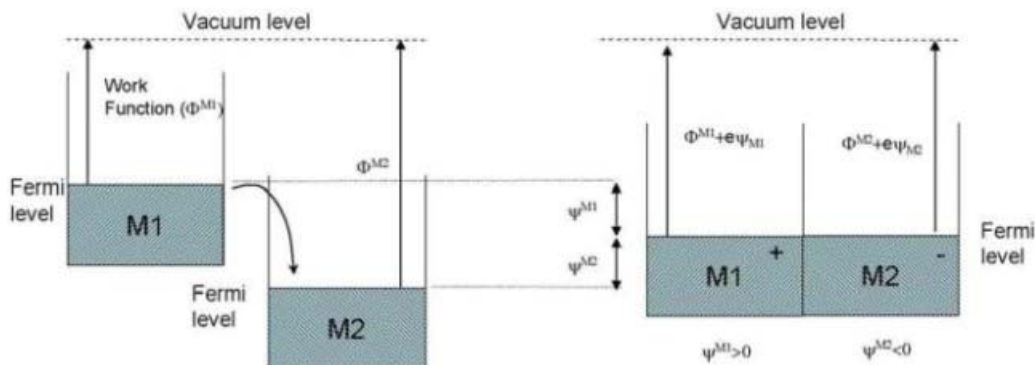


Figure 3. Schematic energy diagram explaining the creation of a potential difference between two metals in contact

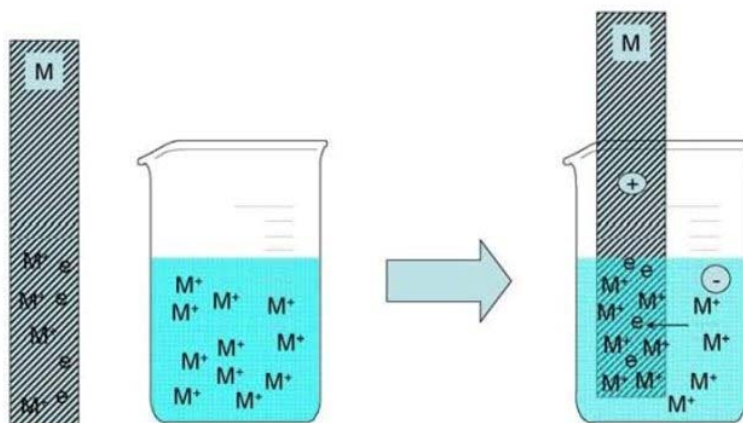


Figure 4. Origin of a potential difference between a metal and a solution

In conclusion, when two phases are in contact and charged species are allowed to travel between them, a potential difference between the phases is created. The purpose of the thermodynamic study of electrochemical systems is to understand the relation between this potential difference and the properties of the system such as the chemical nature of the components, temperature, concentration, etc. One difficulty emerges very early in the treatment of this problem. It is impossible to measure the potential difference between two different phases. The reason for this becomes obvious if we imagine the experiment to measure such potential difference. Let's say we have a piece of metal M in an electrolytic solution and we want to measure the potential difference between the two phases. For this we would use a voltmeter. We would connect one lead of the voltmeter to the metal and the other end to the solution. This is when we find the problem. If we introduce the cable of the voltmeter in the solution we will create a new interphase between the metal that forms the cable and the solution (see Figure 5). In fact, another potential difference will be created between the lead of the voltmeter and the metal M. Then, the potential measured is in fact the addition of at least three potential differences.

The ensemble of the metal piece and electrolyte solution described in the previous

example is commonly called electrode, although it is also customary to use the word electrode to refer only to the metal. It is also customary to use the word potential instead of potential difference. Then the conclusion achieved in the preceding paragraph can be summarized as follows: *it is impossible to measure the potential of a single electrode system.*

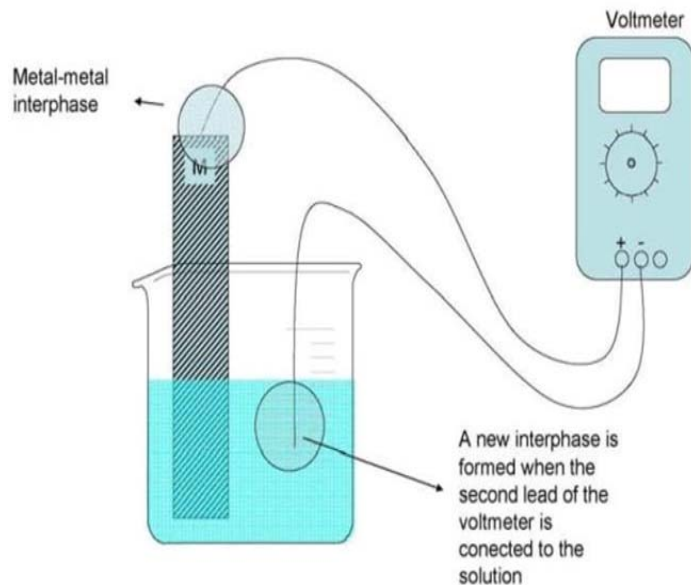


Figure 5. Problem to measure the potential difference between a metal and a solution

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Biographical Sketch

Dr. Victor Climent graduated with first class honors at the University of Alicante in 1995 and obtained his Ph.D. in the same University in 2000. He was awarded a Marie Curie Fellowship for a postdoctoral position in Oxford University under the supervision of Prof. Richard Compton, where he stayed for two years, 2001 and 2002. He returned to the University of Alicante as Ramon y Cajal fellow and became Associate Professor in 2007. His work has focused on the study of the relation between electrode surface structure and reactivity. On this subject he has coauthored more than 60 papers and several book chapters.