



Some future works of research in electrochemistry

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Abstract

From the brief critical overview of such energy conversion processes as fuel cell (FC), electrolysis of water/hydrochloric acid and discharge/charge of lithium ion batteries, and corrosion process with aid of the conception of anodic and cathodic overvoltages, we derived some key unsolved/unanswered questions which are proposed as future key issues of electrochemistry which can be split into 4 thematic issues. Furthermore, 2 issues of energy conversion at “mixing entropy batteries” by reverse electrodialysis/desalination by electrodialysis and solar galvanic cell/reverse photovoltaic cell with a semiconductive organic light emission diode (OLED) are also briefly supplemented.

Keywords Reversibility · Galvanic cell · Local corrosion cell · Reversible intercalation · Reversible de-intercalation · Overvoltage · Polarization · Hydrogen overvoltage

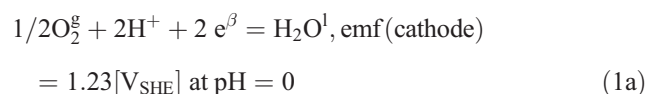
A brief critical overview of such energy conversion cell as self-driven cell, externally driven electrolytic cell, and discharge/charge of Li ion batteries in comparison with local corrosion cells

Let us go back to classical electrochemistry in order to extract the unexplained questions/unsolved problems in modern electrochemistry. First, we take a spontaneous self-driven cell and a reverse externally driven forced cell, a local corrosion cell, and intercalation/de-intercalation of lithium ions to/from metal oxide; study them critically once again throughout theme with respect to two conceptions, reversibility and overvoltage, underlying the key frames of electrochemistry; and finally derive some existing unexplained questions/unsolved problems that are then proposed as future key works in modern electrochemistry.

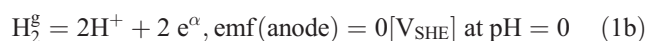
Now we demonstrate the essence of the two concepts with the simple hydrogen-oxygen/chlorine fuel cell (FC), the electrolytic cell, the local corrosion cell, and discharge/charge of

lithium ions battery as noted below. The reversible overall cell reaction is composed of two partial electrode reactions.

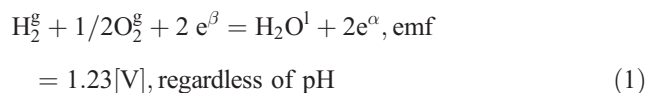
Cathodic partial electrode reaction for a half cell (redox couple):



Anodic partial electrode reaction for another half cell (redox couple):



Total (overall) cell reaction:



, where e^α and e^β are redox electrons of gaseous hydrogen at the anode and gaseous oxygen at the cathode, respectively, which may not cancel each other because of their different electrochemical potentials, even though both redox electrons have one and the same mass and charge [1].

Substituting the redox couple $2\text{H}^+/\text{H}_2$ for $\text{O}_2/\text{H}_2\text{O}$ and Fe^{2+}/Fe for $2\text{H}^+/\text{H}_2$ and then “mixing” the 2 electrode potentials of the 2 redox couples, we get a so-called local corrosion cell which consists of a local anode corresponding, for instance, to a less noble matrix phase with a relatively lower electrode potential and a local cathode, corresponding, for

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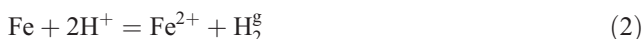
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instance, to a nobler inclusion with a relatively higher electrode potential on one and the same metallic Fe surface.

If the local cathode with an extremely large area is possibly in the immediate vicinity of the local anode with a small area, then dissolution of Fe (corrosion) occurs favorably with a good example of “differential aeration cell” (“iron breathes in and out well with gaseous oxygen to the rust,” provided that the redox couple $2\text{H}^+/\text{H}_2$ is replaced with that redox couple $\text{O}_2/\text{H}_2\text{O}$). This was just against out-of-date corrosion science in earlier days that the large areas of cathodic sites are well protected from corroding the metal. Since the corrosion current follows the law of least resistance, however corrosion will occur in the place close to the passivated cathodic region. So it has even nowadays been called the paradox of corrosion science.

In contrast to Rx 1, irreversible corrosion with gaseous hydrogen evolution in acidic electrolyte can be formulated as follows.

Total (overall) local corrosion cell reaction:

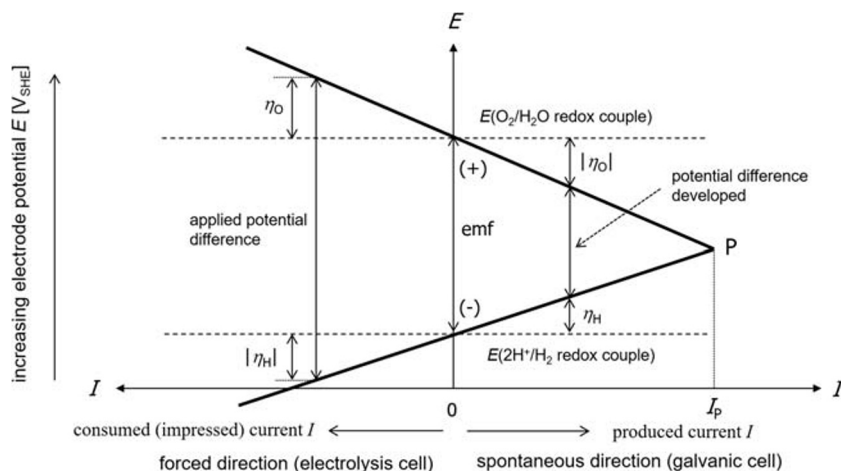


It is noted that in contrast of Rx 1, e^α and e^β involved in Rx 2 must cancel each other because of the same electrochemical potential of both the local anode and cathode [2].

Figure 1 demonstrates the relationship of a self-driven (current-producing) cell (hill-down going energy producing system) to an externally driven (current-consuming) cell (hill-up moving materials producer system) in a solid as well as an aqueous electrolyte with respect to emf (electromotive force) and overvoltage.

Reversibility of the electrochemical cells at I (net current) = 0 for both the galvanic and electrolytic cells implies that external back (counter) emf infinitesimally greater than emf causes an electrolytic cell (backward reaction of Rx 1), but the cell potential smaller than emf gives a galvanic cell (forward reaction of Rx 1). The reversibility can be ensured at any state using a “hypothetical potential source.”

Fig. 1 Comparison in sign of overvoltages, (η) and polarizations (η') between galvanic (current-producing) cell and electrolysis (current-consuming) cell in aqueous electrolytes. The point P represents a local corrosion cell, for which the mixed potential (corrosion potential) of anodic sites and cathodic sites on one and the same metal surface corroding is obtained by substituting the redox couple $2\text{H}^+/\text{H}_2$ for $\text{O}_2/\text{H}_2\text{O}$ and Fe^{2+}/Fe for $2\text{H}^+/\text{H}_2$



For completely (100%) irreversible (spontaneous) electrochemical processes, eventually chemical energy will be released in the form of heat without generating a potential difference; in other words, the potential difference = 0 (between local cathode and anode) at point P is a mixed (corrosion) potential [2].

A reversible process occurs when an intensive variable, such as voltage, opposes externally applied variables. This resembles a tug-of-war between two evenly matched opponents, where the work done by the winner depends upon the resistance they meet, not upon their own inherent strength. By analogy, we can imagine a kind of potential reservoir (a hypothetical potential source) for such a mental experiment.

The overvoltage (overpotential) η or polarization η' is defined as a deviation from a defined reference point, such as the thermodynamic equilibrium, E_{eq} , or the steady-state corrosion potential, E_{corr} , respectively:

$$\eta_c = (E_{delivered} - E_{eq}) \quad (3a)$$

, where cathodic overvoltage $\eta_c < 0$ of a self-driven cell.

$$\eta_a = (E_{delivered} - E_{eq}) \quad (3b)$$

, where anodic overvoltage $\eta_a > 0$ of a self-driven cell.

E_{eq} is physically uniquely defined in value at constant temperature and pressure.

Overvoltage for an externally driven electrolytic cell can be defined as a departure from E_{eq} by substituting externally applied potential for measured/delivered potential for the self-driven cell.

A corrosion cell is within a galvanic cell with a spontaneous reaction, but the overvoltage in the corrosion cell resembles the overvoltage in the externally driven electrolytic cell in a sense of measuring the polarization curve, substituting E_{corr} for E_{eq} . The cathodic overvoltage develops the cathodic branch of the polarization curve, while the anodic overvoltage produces the anodic branch of the polarization curve, starting

at the corrosion potential, E_{corr} . When an external current is impressed, the polarization, η , is then defined by the following equation:

$$\eta'_c = (E_{\text{applied}} - E_{\text{corr}}) \quad (4a)$$

, where the cathodic overvoltage (polarization) $\eta'_c < 0$ of a local corrosion cell.

$$\eta'_a = (E_{\text{applied}} - E_{\text{corr}}) \quad (4b)$$

, where the anodic overvoltage (polarization) $\eta'_a > 0$ of a local corrosion cell.

Note that, for instance, a contribution of charge transfer reaction to overvoltage necessary in a self-driven cell is quantitatively assessed by the charge transfer resistance R_{ct} which is inversely proportional to the exchange current density, i_0 . However, in a local corrosion cell, any contribution of charge transfer reaction to overvoltage necessary is quantitatively assessed by the polarization resistance R_p which is inversely proportional to the corrosion current density, i_{corr} (following the Stern-Geary formula). For either process, inverse proportionality (“the ohmic behavior”) is valid only for low overvoltage limits, $\eta_{\text{ct}} \ll 26 \text{ mV} = \frac{RT}{zF} = \frac{\text{thermal energy}}{zF}$, for $z = 1$.

The strict difference between overvoltage/overpotential, η , and polarization, η' , was first stated by K J Vetter, H Gerischer, and G Kortuem (German Berliner electrochemists) [3] and it is nowadays still traditionally popular in European electrochemical community, while the two terminologies are used in common in Anglo-American community. That means a deviation/departure from the equilibrium state or steady-state and hence an impediment/disturbance of charge transfer reaction (redox reaction) including subsequent or preceding diffusion. In the case of mixed charge transfer reaction and diffusion, the slowest reaction step means just the most strongly impeded/disturbed step with the maximum overvoltage/resistance to that step. That step is termed the rate-determining/controlling step (rds) of the overall reaction concerned [4].

The corrosion potential, which is just an irreversible, non-equilibrium potential at steady-state, is assumed to be formed by “mixing” two electrode potentials of two redox couples, coupled by a common current density which is called corrosion current density or exchange current density. Therefore, the corrosion potential in value, represented by point P on Fig. 1, necessarily lies in a wide range between the two equilibrium potentials being physically well-defined. For instance, the equilibrium potential of pure Fe in solution containing 1 M Fe^{2+} ions at 298 K is $-0.44 \text{ V}_{\text{SHE}}$, regardless of where it is in Germany or USA, or which form it exists in a nano-wire or a sheet or a bulk. The rule always holds for any redox couple.

Since so high cathodic hydrogen overvoltage in absolute value on a nobler metal such as Hg [4, 5] with a high R_{ct} is quite enough to completely block/prevent hydrogen evolution

included in Rx 2, so iron dissolution does scarcely proceed according to Rx 2. For instance, the dissolution rate is extremely low on amalgamated steel and amalgamated Zn electrode in Leclanche cell [5]. However, dissolution rate increases strongly according to Rx 2, in the presence of small amount of impurities of nobler metal with low hydrogen overvoltage such as Pt [4]. It is noted that the cathodic hydrogen overvoltage at E_{corr} definitely means the departure from the equilibrium potential, E_{eq} for the redox couple of $2\text{H}^+/\text{H}_2$, as indicated in Fig. 1.

Strongly adsorbed hydrogen on surface was thought to act as a barrier to corrosion. The removal of adsorbed hydrogen by a depolarizer (an English translation of the original German term of “Depolarisator”), for instance, through entry of oxygen (oxidant), would unblock or depolarize hydrogen adsorbed on surface and hence increase the corrosion rate. The depolarization is assumed to occur as a result of chemical interaction between oxidant and gaseous hydrogen on the metal surface which is not always true.

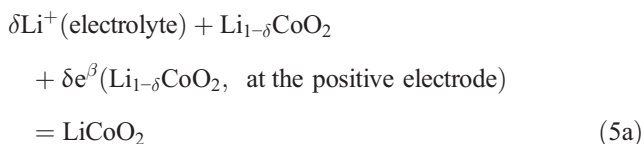
So this is an old fashioned electrochemical conception. The oxidant itself can be reduced instead of reduction of H^+ to H_2 , lowering hydrogen overvoltage. The depolarization is necessarily accompanied by reduction of the hydrogen overvoltage. The term “depolarize/depolarizer” can be interpreted nowadays as lowering the hydrogen overvoltage, thus reducing R_{ct} in value. The short-circuited galvanic cell indicated by point P on Fig. 1 was understood as a depolarized state. So the term “depolarizer” is currently used for a substance that lowers the hydrogen overvoltage by providing a lower R_{ct} .

It is important to note that the mechanism of oxygen reduction in FC may involve either direct reduction via 4-electron transfer or indirect reduction via 2-electron transfer which is now still in doubt [5]. What is more, it turned out that the redox couple $\text{O}_2/\text{H}_2\text{O}$ cannot be used as a reversible electrode, unlike the reversible electrode, $\text{Cl}_2/2\text{Cl}^-$. These two facts are traced back to one reason: O_2 is a chemically very stable compound because it requires high activation energy (a cathodic overvoltage in the self-driven cell) to break its chemical bonds and finally to decompose into oxygen atoms. This high cathodic overvoltage for oxygen reduction resembles that high cathodic hydrogen overvoltage for reduction of hydrogen ions in the corrosion cell.

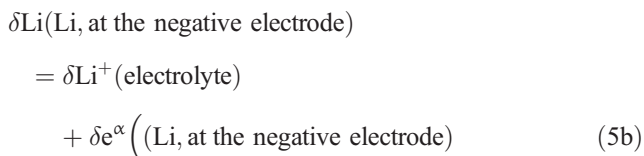
The intercalation/de-intercalation of Li^+ ions to/from $\text{Li}_{1-\delta}\text{CoO}_2$ at the (+) electrode of rechargeable lithium ion batteries is considered a combination of insertion/desertion of Li ions to/from $\text{Li}_{1-\delta}\text{CoO}_2$ with reduction/oxidation of redox couple $\text{Li}_{1-\delta}\text{CoO}_2/\text{LiCoO}_2$, while the de-intercalation/intercalation of Li^+ ions from/to Li at the (–) electrode occurs as a combination of desertion/insertion of Li ions from/to Li with oxidation/reduction of redox couple Li^+/Li [6–8].

Similar to the process shown in Rx 1, the reversible two partial electrode reactions and overall cell reaction of lithium ions battery can be formulated below.

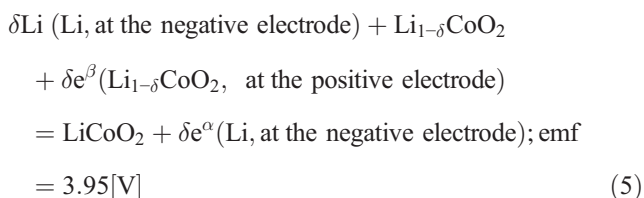
Combined insertion and cathodic partial electrode reaction at the (+) electrode for a half cell (redox couple):



Combined desorption and anodic partial electrode reaction at the (–) electrode for another half cell (redox couple):



Total (overall) cell Rx:



, where e^α and e^β are redox electrons of active mass Li at the negative electrode and those of $\text{Li}_{1-\delta}\text{CoO}_2$ at the positive electrode, respectively, which may not cancel each other [1].

Figure 2 envisages change in the Fermi energy of redox electron, ΔE_F , [$\Delta E_F(1-\delta)$] and [$\Delta E_F(\delta)$] with Li content ($1-\delta$) and (δ) during the discharge and charge, respectively, of a rechargeable lithium ions battery.

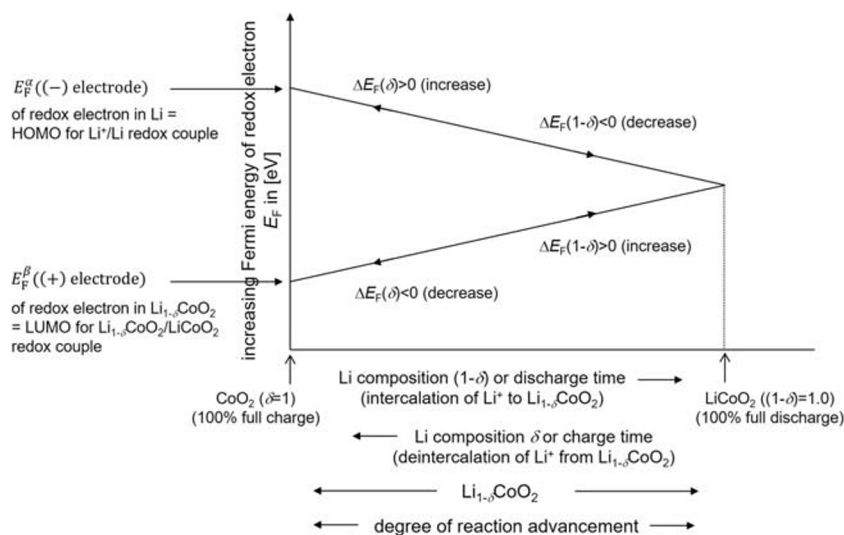


Fig. 2 Change in Fermi energy ΔE_F [eV] of redox electron, e^α and e^β , and $\Delta E_F^\beta(1-\delta)$ at the positive electrode and $\Delta E_F^\alpha(1-\delta)$ at the negative electrode as discharge (intercalation of Li^+ ions to $\text{Li}_{1-\delta}\text{CoO}_2$) proceeds reversibly in a lithium ions battery in a non-aqueous electrolytes. The change $\Delta E_F^\beta(\delta)$ results at the positive electrode, and $\Delta E_F^\alpha(\delta)$

Performing discharge of FC and electrolysis of water/hydrochloric acid, separately, with respect to electrode potential given in Fig. 1, can be compared with one cycle of intercalation/de-intercalation of lithium ions (discharge/charge of the lithium ions battery), with respect to the Fermi energy, presented in Fig. 2. It is readily conceivable that when used in concert, FC (discharge) and hydrogen production cell (charge) are so designed consecutively that such a device permits us to perform one cycle of discharge/charge of advanced FC, similar to “the rocking-chair cell” of rechargeable lithium ion batteries.

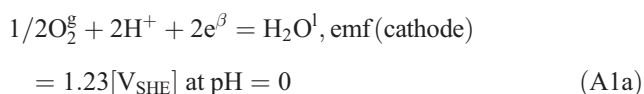
Enumeration of 6 thematic issues derived for future works in electrochemistry

Existing unexplained questions/unsolved problems derived from the critical observations of 4 electrochemical systems being dealt with above can be divided into the 4 categories of thematic issues noted below:

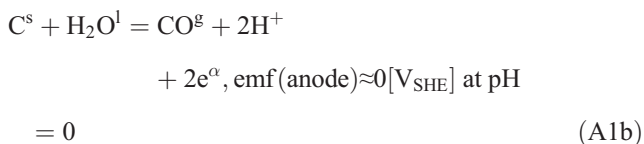
1. Issue regarding FCs (fuel cells)
 - (a) Develop suitable catalysts to reduce the resistance of charge transfer reaction (cathodic overvoltage) as well as diffusion in particular for oxygen reduction in conventional FCs. Note that hydrogen oxidation is not a factor, since relatively low anodic overvoltage is required compared with the high cathodic hydrogen overvoltage in a local corrosion cell.

- (b) A search for suitable anodic and cathodic biomaterials as active mass, including redox couple of electrogenic microbes.
- (c) Develop a new design of rechargeable FCs.
- (d) Electrochemical design of a potential galvanic cell with a thermodynamic efficiency $\eta_{th} > 1$, based upon the chemical reaction $C^s + 1/2O_2^g = CO^g$ with the related entropy change, $\Delta S > 0$; η_{th} is defined as gain, ΔG divided by expenditure, ΔH : $\eta_{th} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$ [5]. η_{th} is mostly less than unity if $\Delta S < 0$ and $\Delta H < 0$ is valid, as is the case for a conventional hydrogen-oxygen/chlorine FC. Such a potential FC comprising two half cells (redox couples) CO/C and O_2/H_2O can be realized as in the following cell configuration:

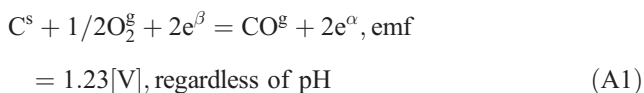
The cathodic partial electrode reaction for a half cell (redox couple):



and the anodic partial electrode reaction for another half cell (redox couple):



Total (overall) cell reaction:



, where e^α and e^β are redox electrons of gaseous hydrogen at the anode and gaseous oxygen at the cathode, respectively, which may not cancel each other [1]. Eventually we calculated $\eta_{th} = 1.25$ at RT for the potential FC mentioned above, using all the existing data available.

2. Issue regarding corrosion

- (a) Develop a monitoring system in conventional cathodic protection and application of anodic protection principle into practice.
- (b) Develop suitable multi-layered oxide and nitride coating materials to enhance the resistance to charge transfer reaction (charge transfer overvoltage) as well as resistance to the coating phase; this is a conventional issue.

- (c) Fabricate semiconducting TiO_2 and V_2O_5 electrodes in the form of nanofilm as a photo anode for a potential application to cathodic protection of stainless steels.
- (d) Clarify the mechanism of corrosion inhibition. In particular determine which active anion species and cation species constituting the inhibitor molecules migrate towards local anodic and cathodic sites, respectively, to passivate the anodic and cathodic surfaces there along with dissolved oxygen/hydrogen ions and metal ions, respectively, thus causing large anodic and cathodic overvoltages, respectively; this is a relatively new issue which requires careful intensive spectroscopic investigation.

3. Issue regarding electrolytic cell

- (a) Develop suitable electrode materials with a high i_0 . For instance, oxide of Ti and V as anodic materials, transition metal oxide, or carbon as cathodic materials, in order to reduce the resistance to charge transfer reaction (anodic and cathodic overvoltages) as well as diffusion in conventional electrolytic processes. Such issues are of great importance in environmental green electrochemistry.
- (b) Electrodeposition of more active metals such as Zn, Ni, and Al, using stable ionic liquids containing electrolytes, in place of aqueous electrolytic solutions containing conventional additives that require a high hydrogen overvoltage.
- (c) Photoelectrolysis of water with $SrTiO_3$ or TiO_2 , acting as a photo-anode, and WS_2 , acting as a photocathode; this is concerned with the processes of energy conversion of light quanta energy into electric energy, recently developed. This is of great importance in energy-saving area. The issue is the same as 6(b) mentioned below.

4. Issue regarding rechargeable lithium ion batteries

- (a) Clarify the mechanism of intercalation/deintercalation using Mg ions in place of Li ions.
- (b) Introduce Li peroxide into active mass at the positive electrode instead of such transition metal oxide as CoO_2 and NiO , provided that oxygen reduction is adopted at the positive electrode during discharge, as in conventional FCs.
- (c) Investigate the role of electron mediators in charge transfer reaction at the positive and negative electrodes to determine how they facilitate combined insertion/desertion of lithium ions and charge transfer reaction, provided that an appropriate electron mediator is available.

Additionally following 2 categories of thematic issues are complemented from the area recently developed as note below.

5. Issues concerning the energy conversion of chemical energy into electrical energy (Fermi energy of redox electron) (reverse electro dialysis) and vice versa (electro dialysis)
 - (a) Develop dialytic batteries (“mixing entropy batteries”) in which energy extraction is based upon the difference in water salinity.
 - (b) Develop desalination using forced electro dialytic processes
6. Issues concerning the energy conversion of light quanta energy into electrical energy (Fermi energy of redox electron) (electrochemical galvanic solar cell) and vice versa (reverse photovoltaic cell)
 - (a) Construct and examine photo-galvanic cell, for instance, using the dye thionine (T) and the redox couples $\text{Fe}^{3+}/\text{Fe}^{2+}$ or I/I^- at the cathode. An issue of reverse photovoltaic cell (conversion of impressed current into light quanta in the form of electroluminescence) using a semiconductive organic light emission diode may be less conceivable for electrochemist to challenge than the former issue of photo-galvanic cell.

Note that a photo-galvanic cell deals mainly with electron transfer at the interface between electrode and electrolytic solution (originating from original L. Galvani’s work) of more interest to electrochemist, while a photovoltaic cell needs to mainly describe electron transfer at the interface between electrode and semiconducting material (originating from original A. Volta’s work) of less interest to electrochemist.

- (b) Photoelectrolysis of water with SrTiO_3 or TiO_2 , acting as a photo-anode, and WS_2 , acting as a photocathode; the issue is the same as 3(c) mentioned above.

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