



# Photo-assisted acid-base machine: Battery ensemble to perform work from neutralization reactions



William G. Morais, Gilberto Lima, Wellington J.A.S. Gomes, Fritz Huguenin\*

Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto – Universidade de São Paulo, 14040-901 Ribeirão Preto, SP, Brazil

## ARTICLE INFO

### Keywords:

Neutralization batteries  
Energy harvesting  
Water splitting  
Oxygen reduction reaction  
Proton electro-insertion

## ABSTRACT

This study proposes a power source that operates between acidic and basic reservoirs under sunlight to treat acidic wastewater sustainably. We present a strategy that harvests energy from an ionic gradient associated with acidic solution neutralization and water photo-oxidation under UV light. In contrast to neutralization batteries, these photo-assisted acid-base machines operate with an interconnected battery ensemble comprising (A) a photo-assisted acid battery composed of photo-anode (TiO<sub>2</sub>) for water photo-oxidation and a selective self-assembled cathode consisting of poly(3,4-ethylenedioxythiophene) and phosphomolybdic acid for proton insertion; (B) a proton-alkali ion battery composed of the self-assembled electrode for proton deinsertion and a cathode made of copper hexacyanoferrate for potassium ion electro-insertion, which can be used as portable or stationary power source; (C) an alkali ion-air battery composed of the polycyanometalate for potassium ion deinsertion and a platinum cathode for the oxygen reduction reaction (ORR). This ensemble avoids reverse water splitting reactions and dismisses the need for external electrical power sources, which increases machine efficiency. Experiments demonstrate that acidic solution neutralization from pH = 1.3 to pH = 6.0 can harvest 102.6 kJ per mol of electro-inserted proton: this process converts energy from sunlight and from ionic gradient into electrical work. Therefore, the strategy presented here may contribute to environmental preservation and sustainable growth.

## 1. Introduction

The development of alternative energy sources to mitigate the pollution generated by fossil fuel combustion has stimulated the search for new ways to convert and to harvest energy. Renewable energy-sourced electricity (RES-E) has attracted worldwide attention for two main reasons: carbon-free electricity generation is a strategy that can abate climate change, and electricity demand is expected to increase up to 80% by 2040. Hydropower, wind power, and solar photovoltaics have dominated RES-E production. The global wind power harvesting capacity and the energy harvested by solar photovoltaic technologies are expected to reach approximately 666 and 400 GW by 2019 and 2020, respectively [1, 2].

Humankind has to find the means to use clean and potable water more effectively. Climate change, pollution, and population growth have raised concern about water scarcity. Nowadays, about 3% of the global electricity is consumed by municipal wastewater treatment plants [3]. Energy harvesting during wastewater treatment should encourage environmental preservation and contribute to sustainable growth: this treatment can be profitable to companies that generate and

treat effluents [4–6].

One strategy to harvest energy is to employ an ionic gradient and then convert it into electrical energy [7–9]. Researchers have recently tested systems that apply electrolytic solutions containing different salt concentrations to deliver work after electrochemical cycles [10–12]. In this context, our group has proposed acid-base machines to harvest energy during acidic solution neutralization, the so-called neutralization batteries, which are an alternative way to treat acidic wastewater sustainably [4, 5, 13, 14].

The working principle of these neutralization batteries encompasses four steps: (1) acidic solution injection; (2) selective proton and anion electro-insertion in the electrodes; (3) base addition to the solution; and (4) proton and anion electro-deinsertion from the electrodes. The resulting saline solution can be discharged in a suitable place, and the cycle can be repeated several times. Although this proposal is a viable means to recuperate the financial investment in wastewater treatment, novel strategies could help to overcome some of the challenges posed by these acid-base machines, enhance energy harvesting, and allow this technology to be implemented. One of the aforementioned challenges is that these batteries require a non-spontaneous electrochemical process

\* Corresponding author.

E-mail address: [fritz@ffclrp.usp.br](mailto:fritz@ffclrp.usp.br) (F. Huguenin).

to complete the electrochemical cycle, which decreases the amount of harvested electrical energy. Another challenge is that acidic solution neutralization does not increase anion concentration, so energy harvesting is only associated with proton concentration change. Although anion electro-insertion/electro-deinsertion in/from a second electrode can selectively occur during the charge/discharge cycles, other electrochemical processes could boost energy harvesting. Finally, finding selective, reversible, and stable electrodes for anion storage represents a third challenge concerning these machines.

Here, we propose an alternative to harvest energy from a photo-assisted acid-base machine comprising an ensemble of three different batteries placed between acidic and basic reservoirs: a photo-assisted acid battery, a proton-alkali ion battery, and an alkali ion-air battery. We present the machine and the batteries only conceptually. To simulate the neutralization process, the amount of energy to be captured (work to be performed by the machine) is based on the electrochemical semi-reactions conducted in electrolytic solutions containing protons and potassium ions.

Anion electro-insertion does not take place in this ensemble, so the photo-electrochemical process under UV radiation substitutes the non-spontaneous electrochemical process applied to neutralization batteries. We use electrodes composed of phosphomolybdic acid (PMA) clusters immobilized on a host matrix consisting of poly(allylamine chloride) (PAH) and poly(3,4-ethylenedioxythiophene-poly(styrenesulfonate) (PEDOT-PSS), which present desirable properties such as low practical irreversibility, proton electro-insertion/electro-deinsertion selectivity, and high polaron conductivity [13, 15–19]. Aiming to achieve low diffusion overpotential and Ohmic drop, we apply the layer-by-layer (LbL) method to grow the thin film [20]. We employ an electrode made of copper hexacyanoferrate (CuHCF) for alkaline metal ion electro-insertion/electro-deinsertion. In this Prussian Blue Analogue (PBA),  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions connected by  $\text{CN}^-$  bridges respectively coordinate to six carbon atoms and to six nitrogen atoms to form  $\text{KCu}[\text{Fe}(\text{CN})_6]$ , which enables hydrated cation insertion/deinsertion [21–23]. Due to their photocatalytic and electrocatalytic properties, we use a photo-anode consisting of  $\text{TiO}_2$  nanoparticles and a platinum sheet for the Oxygen Evolution Reaction (OER) and for the ORR, respectively.

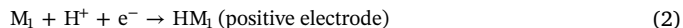
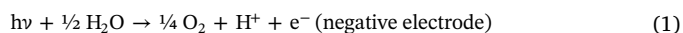
### 1.1. Working principle, work, and efficiency

The proposed photo-assisted acid-base machine involves two host matrices for protons and alkaline metal ions as well as one photo-anode and one catalyst electrode for the OER and the ORR, respectively. The system operates between an acidic and a basic solution to simulate acidic wastewater neutralization. Fig. 1a shows the photo-assisted acid-base machine working principle, and Fig. 1b displays a suggestion for electrode arrangement, where the batteries that compose the machine are defined by connections between these electrodes. The electrochemical cycle involves five steps, three of which are electrochemical (in three different batteries) and two of which involve an open system for the acidic (with simultaneous neutralized solution discharge) and the basic solutions to enter. The operational step sequence is as follows: (I) OER on the photo-anode during water photo-oxidation in acidic medium and proton electro-insertion in the host matrix  $M_1$ , which corresponds to photo-assisted acid battery discharge; (II) injection of base from the basic reservoir into the electrolytic solution; (III) proton electro-deinsertion from the host matrix  $M_1$  and alkaline ion electro-insertion in the host matrix  $M_2$ , which corresponds to proton-alkali ion battery discharge; (IV) neutralized solution discharge in a suitable environment and injection of acidic solution from the acidic reservoir; and (V) alkaline ion electro-deinsertion from the host matrix  $M_2$  and ORR in the electrocatalyst, to result in the alkali ion-air battery discharge. After the last step, the cycle is repeated as long as there is acidic solution in the reservoir.

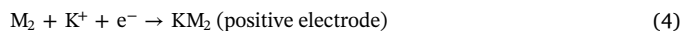
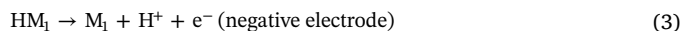
Below we show the batteries and electrochemical reactions at the

negative and positive electrodes.

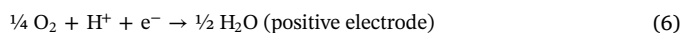
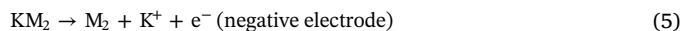
Step I: Discharge of the photo-assisted acid battery.



Step III: Discharge of the proton-alkali ion battery.



Step V: Discharge of the alkali ion-air battery.



From steps I to V, note that the photo-assisted acid-base machine does not correspond to coupling of the separate batteries. Actually, the batteries are interconnected, once the  $M_1$  and  $M_2$  electrodes participate together in one battery (proton-alkali ion battery) only, and each of them participates in another battery ( $M_1$  in the photo-assisted acid battery and  $M_2$  in the alkali ion-air battery) during the complete electrochemical cycle. These interconnections are necessary to achieve our goal: to convert energy from sunlight and from ionic gradient (associated with neutralization) into electrical work.

In fact, free energy variation (mainly change in entropy) is associated with proton and alkaline ion concentration change due to neutralization: protons and alkaline ions are removed from the concentrated medium (acidic and neutral solutions in Eqs. (2) and (4), respectively) and added in the diluted medium (neutral and acidic solutions in Eqs. (3) and (5), respectively).

In contrast to conventional water splitting, the Hydrogen Evolution Reaction (HER) does not directly consume the protons generated by the OER in this system. Instead, a selective host matrix captures the protons and releases them after neutralization in less acidic or neutral medium. Hence, water photo-oxidation (without the HER) charges the proton-alkali ion battery and, after neutralization (step II), this battery is discharged in neutral medium (step III). This methodology presents other advantages: (1) molecular hydrogen storage is difficult to accomplish, and energy is stored when protons are inserted in the photo-assisted acid battery cathode; (2) reverse water splitting reactions associated with molecular hydrogen and molecular oxygen evolving from water splitting are avoided [24], to increase conversion efficiency; and (3) the proton-alkali ion battery can be removed and used as a portable power source, which can be charged again when its  $M_2$  positive electrode is electro-oxidized during the alkali ion-air battery discharge (step IV), and its  $M_1$  negative electrode is electro-reduced in the photo-assisted acid battery (step I) in the next electrochemical cycle. Note that advantages (1) and (2) mentioned above could also be obtained if we exchange the positive electrode of step I for the negative electrode of step V (or if we exchange the negative electrode of step V for the positive electrode of step I) and exclude steps II, III, and IV. However, here we could not harvest energy from the change in concentration associated with neutralization to reach our main objective – to contribute to environmental preservation and sustainable growth.

To determine the useful maximum work produced by this machine due to change in concentration associated with neutralization, which corresponds to mixture free energy (mainly mixture entropy) at constant pressure and temperature, we consider isothermal, buffered, and reversible steps. Moreover, we consider that no heat is dissipated during the electrochemical steps, and we are not interested in harvesting energy from heat neutralization. To determine the mixture free energy associated with the change in proton and alkaline ion concentration, we use the Nernst's equation to determine the electromotive forces for the insertion/deinsertion processes.

According to Eqs. (2) and (3), the  $E_1^a$  and  $E_1^n$  equilibrium potentials of these electrochemical reactions can be determined by  $\text{H}^+$  ( $a_{\text{H}^+}$ ),  $M_1$

Download English Version:

<https://daneshyari.com/en/article/6661620>

Download Persian Version:

<https://daneshyari.com/article/6661620>

[Daneshyari.com](https://daneshyari.com)