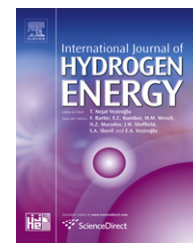


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# Oxygen evolving reactor overpotentials and ion diffusion in photo-catalytic and electro-catalytic hydrogen production

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## ABSTRACT

This paper examines the oxygen evolving reaction of water splitting under practical conditions which simulate those encountered in photo-initiated or electrochemical water oxidation processes. Most of the over-potentials are due to electrochemical processes at the anode, where oxygen evolution occurs. This paper investigates the oxygen evolving half cells for different complete systems including photoelectrochemical, photo-catalytic and electro-catalytic water splitting. An electrochemical model is developed to evaluate the over-potential losses in the oxygen evolving reaction and the effects of key parameters are analyzed. The transient diffusion of hydroxide ions through the membrane and bulk electrolyte are modeled and simulated for improved system operation. The results of the thermodynamic and electrochemical analyses show that for each water splitting configuration, there are optimal values of the operating parameters such as electrolyte concentration, current density, and membrane-electrode distance. The operating criteria of key parameters and the optimal working region of the oxygen evolving reactor are examined for assessment and optimization of a complete water splitting system. The analysis of the oxygen evolving reaction is performed for three variations of ruthenium based supramolecular complexes and molybdenum-oxo catalysts for catalytic hydrogen production.

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## 1. Introduction

Hydrogen has emerged as an attractive candidate for a clean, sustainable fuel and underpins an intense interest in creating sustainable systems that use catalysts based on elements abundant in the Earth to achieve efficient hydrogen production from water [1–3]. In order to develop an economical and sustainable pathway, hydrogen should be produced from a renewable energy source, such as solar energy. Photo-

catalytic water splitting is considered to be one of the most promising technologies for this purpose, since hydrogen could be obtained directly from abundant and renewable water and sunlight. If successfully developed with economic viability, this could become the ultimate clean energy technology that could solve future energetic and environmental problems [4–6].

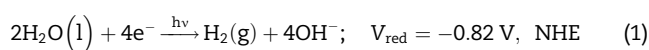
Production of hydrogen in a regenerative fashion such as photochemical splitting of water has been studied extensively [1]. The reductive part of this process requires the development

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of catalysts that promote the reduction of protons to molecular hydrogen, facilitated by direct excitation by a photo-sensitizer. Recently, molecular platinum- and palladium-based systems have been developed as heterogeneous catalysts [7,8]. Supramolecular complexes for photocatalytic hydrogen production that result in high turnover rates and numbers are another area of growing interest [9]. The long lived metal-to-ligand charge-transfer (MLCT) excited state of  $[\text{Ru}(\text{bpy})_3]^{2+}$  has motivated photochemical and photophysical studies for light to energy conversion processes [10,11]. The MLCT excited state of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and its analogs have the required energy to split water into hydrogen and oxygen, but it requires complicated multi component systems for operation.

One of the most promising areas is the development of photochemical water splitting using supramolecular devices, which are able to capture the incident solar radiation, and generate electrons or holes at the active center where water reduction or oxidization occurs. Such systems mimic natural photosynthesis and mainly consist of supramolecular complexes of organic molecules which possess active metallic centers [12]. In this regard, the water photo-reduction reaction occurs as follows:



Compared to hydrogen production methods based on fossil fuels, the high investment cost of solar hydrogen generation is a challenging issue. Therefore, efficient electro-catalytic hydrogen production is needed for a viable short-term alternative. Recently, an efficient and inexpensive catalyst based on molybdenum-oxo complexes has been developed to catalytically generate gaseous hydrogen either from water at neutral pH or seawater [13]. The heterogeneous solution of molybdenum-oxo complexes dissociates the water molecules to hydrogen and hydroxide ions, as indicated in Equation (1).

In order to have a complete system for continuous production of hydrogen, the  $\text{OH}^-$  ions should travel through the electrolytic solution to the anode where oxygen is formed. The hydrogen remains in the catalyst solution. Hydrogen is then separated from water in a gas–liquid separation unit outside of the electrolyser. The transfer of hydroxide ions from the hydrogen evolving reactor to the oxygen evolving reactor and decomposition of these ions to constituent molecules are necessary processes to avoid any rate limiting effects. The hydroxide ion decomposition at the anode occurs based on following reaction:



Most investigations on catalytic hydrogen production focus on the development of new catalysts [14,15], and development of new membrane electrolytes [16]. However, there has been a lack of thermodynamic-electrochemical modeling analyses on oxygen evolving half-cells for a complete system analysis of catalytic hydrogen production. This is important for better understanding of its working mechanisms as well as design optimization. Ni et al. [17] developed an electrochemical model has been to provide the current–voltage ( $J$ – $V$ ) characteristics of the PEM electrolyser. Gerischer [18,19] examined the kinetics and energetics of electron transfer across semiconductor/electrolyte junctions and the nature of the space-

charge layer in the semiconductor layer adjacent to the semiconductor/electrolyte interface. Nevertheless, a systematic and integrated transient phenomenological model is needed for a better understanding of the phenomena occurring in a complete cell and how they contribute to its performance.

In this study, a comprehensive analysis is conducted to investigate the thermodynamic and electrochemical performance of an oxygen evolving reactor that is integrated with a catalytic hydrogen production reactor. An electrochemical model is developed to quantify the over-potential requirements of the OER under various conditions. Also, a transient phenomenological model for ion transfer in the OER is presented. This model aims to develop a better understanding of the ion transfer phenomena occurring in a complete system and how it contributes to electrochemical cell performance.

## 2. Model of irreversibilities and ion transfer

### 2.1. Electrochemical cell model

The electrochemical cell performance of the oxygen evolving reactor, including individual ohmic, activation, and concentration overpotentials, will be formulated. In the water splitting system, the required voltage  $E$  is larger than the reversible voltage,  $E_{\text{rev}}$ , because of the irreversibilities resulting from the water splitting reactions. They are expressed as,

$$E = E_{\text{rev}} + U_{\text{act}} + U_{\text{con}} + U_{\text{ohm}} \quad (3)$$

where  $U_{\text{act}} = \frac{RT}{\alpha n_e F} \ln\left(\frac{j}{j_0}\right)$  is the activation overpotential loss related to the electrochemical kinetics [20],  $j_0$  is the exchange current density specified for an electrode, and  $n_e$  is the number of electrons;  $U_{\text{con}} = \frac{RT}{\alpha n_e F} \ln\left(\frac{j_L}{j_L - j}\right)$  is the concentration overpotential loss caused by mass transfer [20],  $j_L$  is the limiting current density;  $U_{\text{ohm}} = j \frac{t_{\text{el}}}{k}$  is the ohmic overpotential loss caused by the resistance of electrolyte as the resistance of electrodes are negligible compared with the electrolyte [21],  $t_{\text{el}}$  is the thickness of the KOH electrolyte, and  $k$  is the specific conductivity of the KOH solution. All constant values are shown in Table 1.

Based on the following correlation, developed by Gilliam et al. [22], the relationship between the specific conductivity of

**Table 1 – The inputs and fitting parameters used in the present study.**

Parameter	Value	Reference
$A$	0.5	[17]
$D_{\text{OH}^-}$	$5.26 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	[23]
$j_{0(\text{Ni})}$	$6 \times 10^{-6} \text{ A cm}^2$	[24]
$j_{0(\text{G})}$	$4.6 \times 10^{-5} \text{ A cm}^2$	[25]
$j_{L(\text{Ni})}$	$400 \text{ mA cm}^2$	[24]
$j_{L(\text{G})}$	$150 \text{ mA cm}^2$	[25]
$n_{\text{OH}^-}^{\text{init}}$	1 M	NA
$\mu_{\text{O}(\text{OH}^-)}$	$20.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	[26]

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