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# Asymmetric cell design for decoupled hydrogen and oxygen evolution paired with V(II)/V(III) redox mediator

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## ABSTRACT

The electrolysis of water using renewable energy inputs is a promising sustainable approach to produce clean hydrogen fuel. The conventional water electrolysis, where the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are tightly coupled to satisfy the thermodynamic potential of at least 1.23 V, occasionally encounters gas crossover through the membrane, resulting in the formation of explosive gas mixtures and reactive oxygen species. In this study, an asymmetric cell design of 3 M H<sub>2</sub>SO<sub>4</sub>|V(II)/V(III)|1 M KOH equipped with nickel foam electrodes is used for achieving decoupled HER and OER under kinetically favorable conditions by dividing the process into two steps using vanadium ions as redox mediators. The actual overall water splitting at an average cell voltage of 1.3 V and a current density of 10 mA cm<sup>-2</sup> is accomplished even in the presence of membranes with outstanding cycling stability. The well-designed system for decoupled water electrolysis can allow the production of clean energy fuel using a low-power input in renewables-to-hydrogen conversion.

## 1. Introduction

As an ideal energy carrier, hydrogen is considered a promising candidate to overcome environmental issues. Therefore, the sustainable production of hydrogen powered by renewable energy inputs is a green approach to support the hydrogen economy [1–4]. Among the several technologies to produce hydrogen, including thermolysis, biomass, and direct photosynthesis, electrochemical water splitting, which can be combined with diverse renewable energy sources, is believed to be the most promising environmental pathway in the future [3,5–8]. The hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are tightly coupled in conventional water electrolysis, simultaneously producing hydrogen and oxygen. These are typically conducted using a large voltage input (1.8–2.5 V) under either acidic or alkaline conditions at elevated temperatures despite the use of several types of noble metal catalysts because of the sluggish kinetics of water splitting [9,10]. In addition, the simultaneous generation of hydrogen and oxygen allows the possibility of gas crossover through the membrane, particularly at low current densities, resulting in the formation of reactive oxygen species and explosive gas mixtures, which can attack the cell component [11,12]. These limitations of conventional electrochemical water splitting require the development of more efficient

electrolysis systems in which the HER and OER can occur at different times and spaces for the large-scale production of hydrogen.

To produce hydrogen and oxygen at separate times during water electrolysis, the decoupling strategy for water splitting, where an electron-coupled-proton buffer (ECPB) is used as a type of redox mediator, was proposed by Symes and Cronin in 2013 [13]. Using polyoxometalate as a redox mediator, a total voltage of 2.94 V was achieved at 100 mA cm<sup>-2</sup>, which was comparable to that for single-step water electrolysis (2.55 V at 100 mA cm<sup>-2</sup>). Since then, numerous studies on decoupled water electrolysis have been conducted using representative proton-dependent redox mediators including hydroquinone sulfonate [14], silicotungstic acid [15], and vanadium species [16], as well as solid-state redox mediators such as NiOOH/Ni(OH)<sub>2</sub> [17]. However, most of these redox mediators perform well only in strong acidic media, thus limiting the use of suitable electrocatalysts, particularly for the OER, owing to the facile degradation of the earth-abundant transition-metal-based OER electrocatalysts in acidic electrolytes [9,18].

Herein, an asymmetric cell design is proposed and constructed for decoupled hydrogen and oxygen evolution paired with a V(II)/V(III) redox mediator in kinetically preferred media—acidic for HER and alkaline for OER [19]. By combining the synergistic advantages of the cell design comprising an acid/alkaline dual solution and a V(II)/V(III)

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