Redox Mediated and Decoupled Water Electrolysis Using Soluble Inorganic Mediators: A Comprehensive Review

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***Abstract*—The worldwide trend toward the green energy systems has enhanced academic research into the biological synthesis of green hydrogen through the electrolysis of water. Conventional electrolytic systems require simultaneous Hydrogen Evolution Reaction and Oxygen Evolution Reactions that are separated by ion-exchange membranes; such systems are prohibitively expensive, complex to operate, and their lifetime is limited.**

Decoupled and redox-, redox-, and electrolysis Redox can now be utilized as a promising paradigm, with redox couples being used as electron shuttles to either spatially or temporarily separate Hydrogen Evolution Reaction and Oxygen Evolution Reaction to allow membrane-free systems or scalable multi-reactor systems. This paper critically reviews the current developments in the field of mediated and decoupled water electrolysis with a focus on Ferri/ferrocyanide systems used in alkaline water and chromium-based mediators used in acidic water. Systematic analyses are made of rationalizations of reaction mechanisms, thermodynamic viabilities, kinetic profiles, material choices, performance metrics, safety considerations, and scalability issues.

Comparative evaluation with other possible mediator systems including iodine, cerium, and manganese couples is made, and the merits and limitations of each of the systems are brought to light. The discussion highlights the opportunities to achieve cost-efficient hydrogen production on a laboratory scale and outlines the relevant research gaps that should be filled to take these technologies to the next stage of practical and industry-deliverable application.

***Index Terms*—Decoupled water electrolysis, Redox mediated electrolysis, Hydrogen evolution reaction (HER), Membrane-less electrolysis, Ferri/Ferrocyanide redox couple, Electrochemical hydrogen production**

I. Introduction

Working on hydrogen is often seen by most as a component of future low-carbon energy systems because of its high gravimetric energy density and clean burning characteristics [1]. The renewable electricity-powered water electrolysis provides a long-term solution to hydrogen production; however, traditional alkaline, proton-exchange membrane (PEM), and anion-exchange membrane (AEM) electrolyzers face issues related to cost of the membrane, gas crossover, catalyst degradation, and complexity of the system engineering [2].Specifically, the oxygen evolution reaction (OER) is a reaction, which is slow, energetically active, and adds significantly to the overall cell overpotential [3].

Another potential emerging paradigm is redox-mediated and decoupled electrolysis where the OER is replaced or temporarily separated by a reversible redox couple that is able to store and release electrons [4]. In such setups hydrogen and oxygen do not necessarily have to be produced simultaneously or in the same reactor, dramatically reducing the risk of gas-crossover and allowing the use of membrane-free operation.

This concept has been gaining academic interest since the last ten years as one of the means to reduce system cost, increase safety and offer an opportunity to operate with flexibility [5].

This is a critical review of the recent experimental and conceptual developments in the redox-mediated electrolysis of water, but specifically focusing on two examples, namely,

1. Ferri/ferrocyanide-mediated membrane less water electrolysis in alkaline solution using stainless-steel electrodes
2. Ferri/ferrocyanide-mediated membrane less water electrolysis in alkaline solution using nanoparticle electrodes.
3. Dichromate-mediated decoupled electrolysis in an acidic system.The systems represent the potential and the constraints that are associated with soluble inorganic hydrogen generation mediators.

II. Fundamentals of Redox-Mediated and Decoupled Electrolysis

1. Conceptual Framework

In standard water electrolysis, both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) occur simultaneously at the anode and cathode respectively, thus, requiring a separator to preclude the interactions between hydrogen and oxygen [6]. The oxidation or reduction of a soluble redox species that can be faster kinetically and with lower over potential replaces the anodic OER in mediated electrolysis. In fully decoupled systems, HER and OER are conducted in two different reactors which are connected only by redox mediator cycle [7].

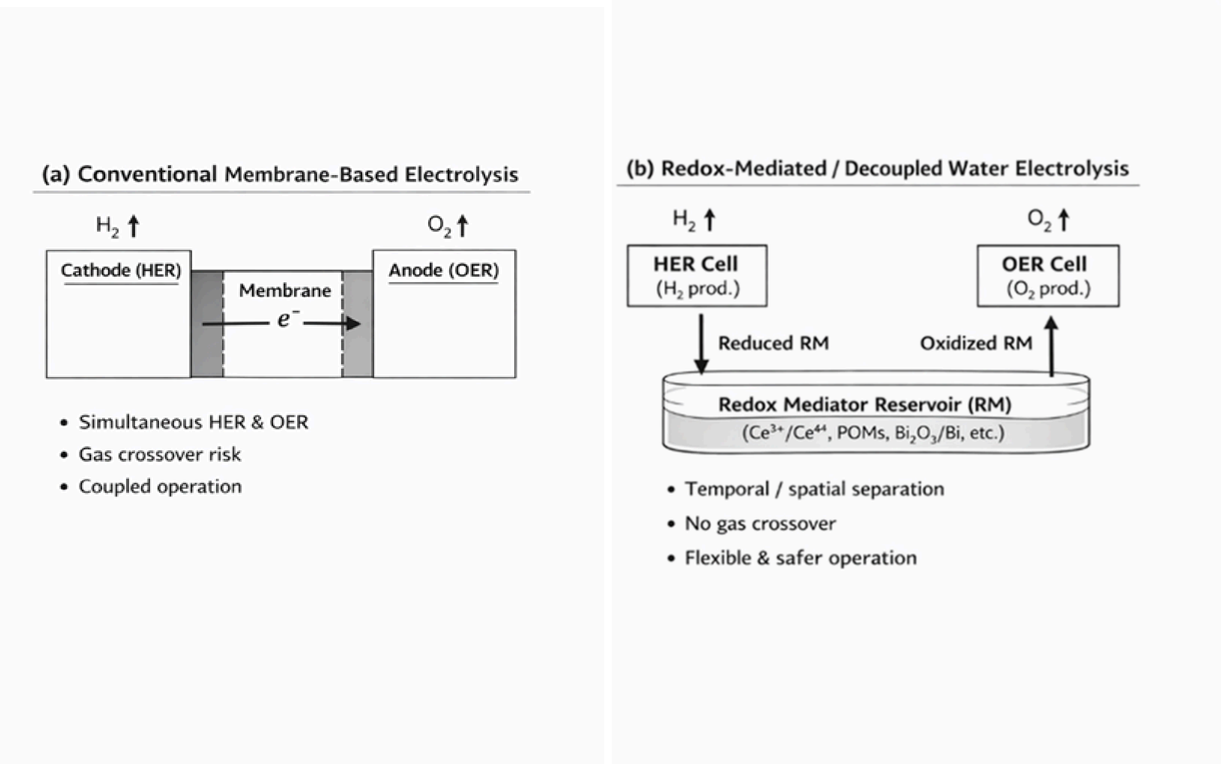


Figure 1: Schematic Comparison of Conventional Membrane Based and Redox-mediated (decoupled) water electrolysis

2. Thermodynamic Relations

Knowledge of the appropriateness of a redox mediator is dictated by its standard redox potential, stability window, solubility and reversibility. Preferably, the redox potential of the mediator must be between that of HER and that of OER to minimize the sum of the cell voltage and yet have enough driving energy [8]. Also the redox chemistry of the mediator should be matching to the pH that the electrolyte surroundings are supposed to be [9].

III. Ferri/Ferrocyanide mediated Membrane-less Electrolysis in Alkaline Media

1. The Redox chemistry and the Redox reaction mechanism

Ferri/Ferrocyanide redox couple Fe (CN)63-/Fe (CN)64- can replace the oxygen-evolution reaction (OER) at the anode in alkaline media and thus allows the operation of the membrane-free mode [10].

Cathodic reaction (HER, alkaline):

$2H_2O + 2\,e^- \rightarrow H_2 + 2OH^-$

Anodic reaction (mediator oxidation):

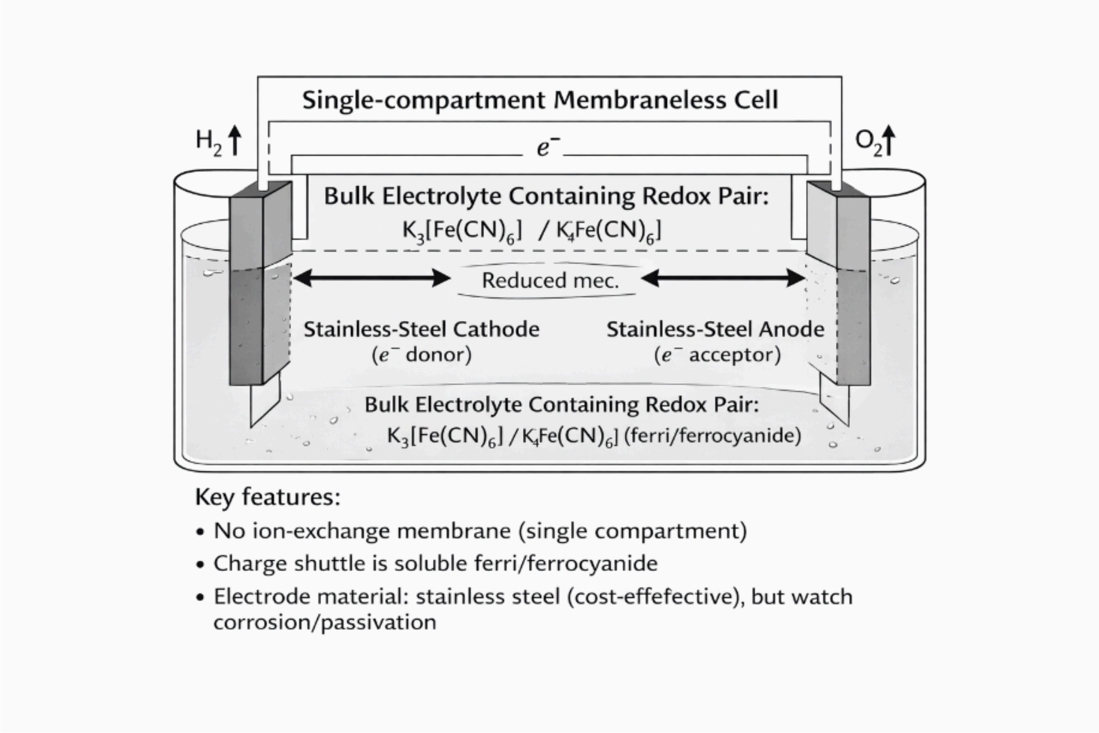
$Fe\,(CN)_6^{4-} \rightarrow Fe\,(CN)_6^{3-} + e^-$

Overall reaction (per 2 e^-):

$2H_2O + 2Fe\,(CN)_6^{3-} \rightarrow H_2 + 2OH^- + 2Fe\,(CN)_6^{4-}$

2. Materials and Cell Design

The stainless-steel electrodes (SS -304/316) are widely used due to low cost, resistance to corrosion in alkaline environment, and moderate hydrogen-evolution reaction. The use of a single-compartment cell bypasses the need to use ion-exchange membranes and hence simplifies the reactor architecture and reduces ohmic dissipation. Common electrolytes include 0.1–1.0M KOH with the presence of dissolved potassium ferricyanide.



Key features:

- No ion-exchange membrane (single compartment)
- Charge shuttle is soluble ferri/ferrocyanide
- Electrode material: stainless steel (cost-effefective), but watch corrosion/passivation

Figure 2: Membrane-less Redox Shuttle-Assisted Electrolysis for Decoupled H_2 and O_2 Evolution

3. Electrochemical Performance

It is an electrochemical performance that measures the capacity of the electrode in relation to the voltage and current of the cell case.

The recorded polarization characteristics have shown significantly low cell voltages as compared to traditional water electrolysis at the same current densities. The cathode generates hydrogen and, the anode is gas-free, and this increases safety. Laboratory Separate demons have identified Faradaic efficiencies virtually near to unitary [11].

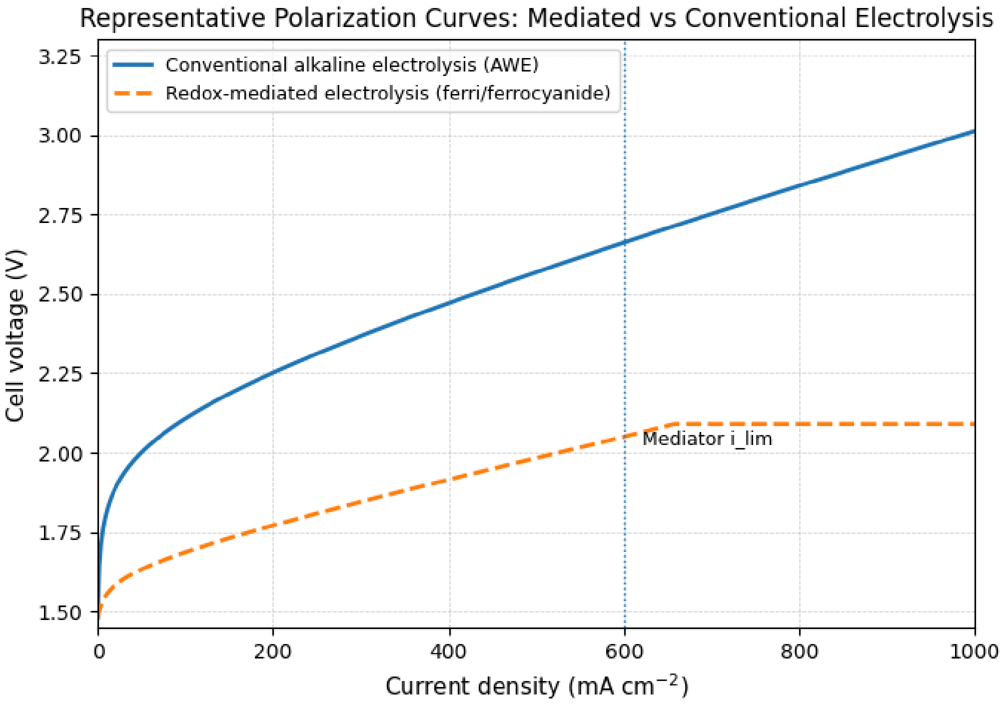


Figure 3: Representative Polarization Curves Comparing Conventional Alkaline Water Electrolysis and Ferri/Ferrocyanide-Mediated Electrolysis

4. Durability and Safety Assessment

Even though the Ferri/ferrocyanide systems exhibit good short-term reversibility, the stability of the system at longer distances might be compromised by photodecomposition and also by the degradation of the ligands. The alkaline media should be strictly kept to ensure that there is no emission of hydrogen cyanide when the environment is acidic. Thus, these restrictions limit scalability, but they are not the reason to deny the utilization of such systems in a laboratory or educational environment *(M. Stern et al.)*.

IV. Potassium Dichromate based Decoupled Electrolysis in Acidic Mediums

1. Chromium Redox Chemistry

Cr (VI)/Cr (III) redox pair possesses a fairly large standard potential (EO ≈ +1.33V vs. SHE), meaning that it can be thermodynamically compatible with the hydrogen evolution reaction (HER) in acidic conditions [13]. The dichromate-based systems are traditionally used in a full decoupled, two reactor system unlike ferricyanide such as the half-reaction [14-18].

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$.

2. Decoupled Reactor Configuration

A common system comprises of an electrochemical reduction reactor (ERR) that produces hydrogen along with the reduction of Cr (VI) to Cr (III). Subsequently, the Cr (III) is re-oxidized in an electrochemical oxidation reactor (EOR) to Cr (VI) and oxygen is generated [19].Temporal separation enables independent optimization of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).

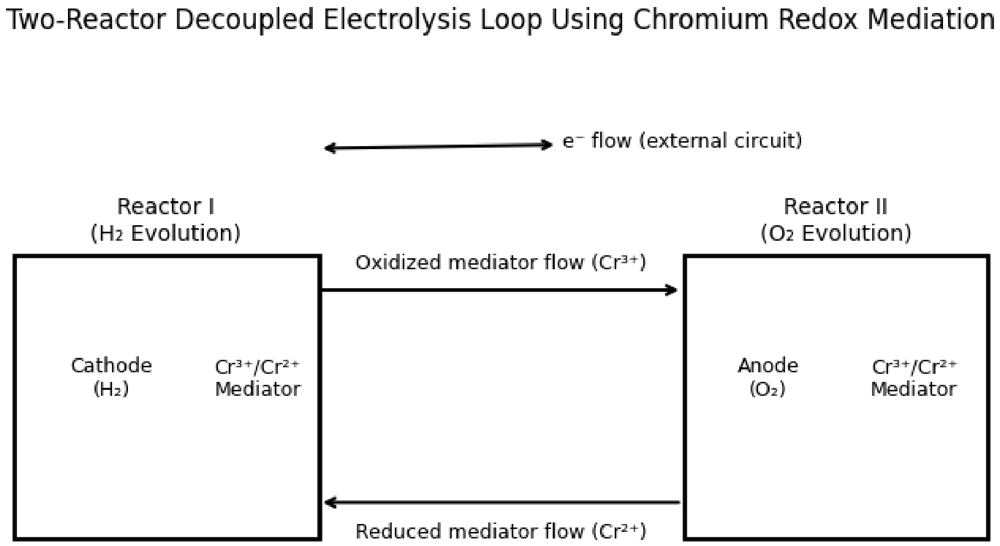


Figure 4:Schematic Representation of a Two-Reactor Decoupled Water Electrolysis System Employing a Cr^{+3}/Cr^{+2} Redox Mediator

3. Performance Metrics

An experimental study seems to show the hydrogen producing step to be conducted with relatively low cell voltages with the hydrogen produced being of high purity [20]. This does not mean that the energy consumption is any lower than that measured in present state-of-the-art PEM systems but, as such results do show, does support the fact that what is being proposed is conceptually possible as well.

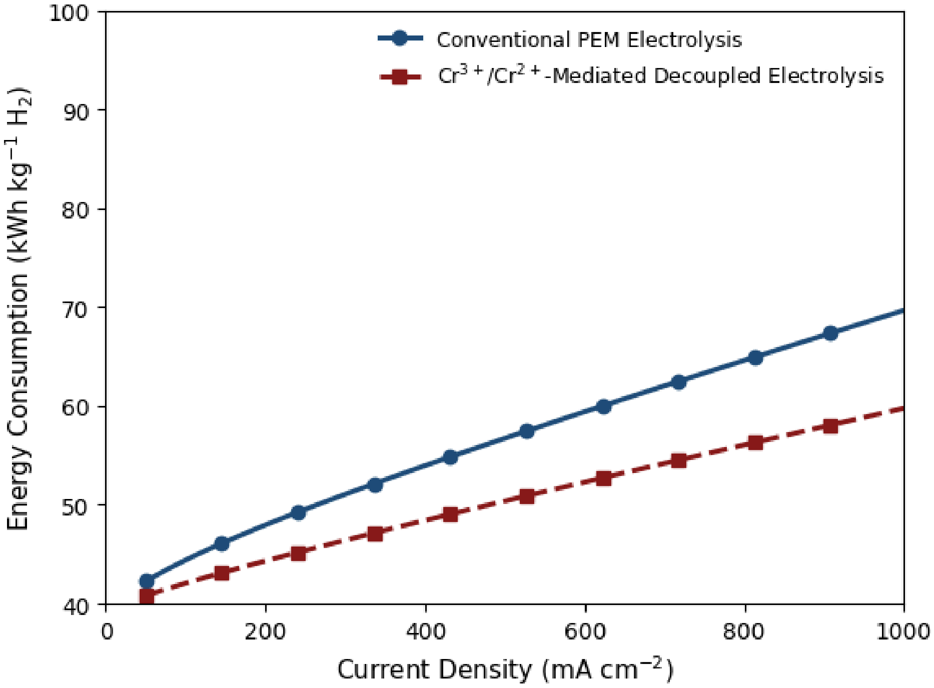


Figure 5: Comparative Energy Consumption of Conventional PEM Electrolysis and Cr^{+3}/Cr^{+2}-Mediated Decoupled Electrolysis as a Function of Current Density

4. Toxicity and Environmental Impact

Although the compounds of the Cr (VI) have favorable electrochemical properties, they are very toxic and carcinogenic [21]. As a result, their implementation requires strict containment and constant monitoring of their use, and full waste-treatment systems. In this regard, di-chromate based systems should be more applicable in mechanistic investigations than in large scale production of hydrogen [22].

V. Comparison to other Redox Mediator Systems

Other mediators have been explored such as I3-/I-, Ce4+/Ce3+, and MnO2/Mn2+. Mediators have unique trade-offs in redox potential, reaction kinetics, cost and environmental impact [23-26]. The ferricyanide is described as a safe, operationally simple chemical in alkaline environments and chromium as a high driving force in acidic systems although increased toxicity.

Table-1: Selected Redox Couples and Their Electrochemical Properties Relevant to Decoupled Water Electrolysis

Redox Couple	E°(V vs SHE)*	Typical Electrolyte / pH	Advantages	Primary Limitations
Fe $(CN)_6^{3-/4-}$	0.36	Neutral–mild alkaline aqueous media	Fast outer-sphere kinetics; high reversibility; well-characterized electrochemistry	Ligand instability under extreme pH; cyanide-related safety considerations

Fe^{3+}/Fe^{2+}	+0.77 (acidic)	Acidic to near-neutral aqueous media	Abundant; low cost; scalable redox chemistry	Hydrolysis and precipitation at elevated pH; corrosion concerns
V^{3+}/V^{2+}	System dependent	Acidic electrolytes	Multi-electron redox chemistry; compatibility with flow systems	Speciation complexity; air sensitivity; higher material cost
Cr^{3+}/Cr^{2+}	–0.41 (acidic)	Acidic media	High theoretical redox capacity; enables spatial decoupling concepts	Cr^{2+} instability; toxicity and environmental constraints
Quinones / TEMPO (organic mediators)	Tunable (0–1.0)	Neutral–acidic media	Molecular tunability; metal-free systems; adjustable redox potential	Chemical degradation; membrane crossover; long-term durability issues
Polyoxometalates (POMs)	System dependent	Acidic–neutral	Multi-electron storage capability; structural robustness	Cost; solubility limitations; electrolyte compatibility

VI. Challenges, Research Gaps and future Outlook

The key challenges for mediated and decoupled electrolysis include

1. Degradation of mediators
2. Crossover induced performance degradation in looped system
3. Energy efficiency concerns and environmental constraints

Future research should focus on finding benign, earth-abundant mediators that show quick kinetics and long-term stability, and, at the same time, search the way to integrate them with renewable sources of energy [7]. It can be the case that hybrid strategies that are synergistic in the fusion of solid and soluble mediators can offer promising prospects of progress.

VII. Conclusions

A promising alternative to more conventional membrane-based processes could be redox mediated and decoupled water electrolysis in terms of cost effective, flexible and safe hydrogen production at the laboratory and pilot scale. Paradigmatic cases such as Ferri/ferrocyanide and dichromate systems can be used to outline the benefits as well as the natural limitations of the soluble inorganic mediators. Current advances in mediator chemistry, reactor design and safety technology are essential to the realization of the potential of this new electrochemical paradigm [5].

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