

Screening aqueous organic redox couples for spontaneous hydrogen generation on catalysts

September 2024

Soowhan Kim Jong-Hwa Shon Litao Yan



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Abstract

Two low-cost redox couples with near neutral or alkaline pH – 7,8-dihydroxyphenazine-2-sulfonic acid (DHPS) and ethylenediaminetetraacetic acid chelated chromium (Cr-EDTA) with ammonia – are identified to generate hydrogen evolution spontaneously on Pt/C catalysts. Cr-EDTA redox couple has two times higher hydrogen evolution rate than that of DHPS, and the charged Cr-EDTA molecules are fully utilized to generate hydrogen gas, while ~ 50% of DHPS molecules are utilized to produce hydrogen spontaneously on Pt/C catalysts. The Cr-EDTA electrolyte enables cost reduction by allowing cheap raw material of Cr and corrosion resistant alloy instead of costly superalloy for catalytic reactor systems. Furthermore, the Cr-EDTA with ammonia as a negolyte for flow batteries is validated to suppress hydrogen evolution side reaction, reaching coulombic efficiency of 99% in flow cell operation paired with [Fe(CN)₆]^{3-/4-} redox couple near neutral pH.

Summary

This project explores feasibility of aqueous organic redox couples to provide spontaneous hydrogen evolution on catalysts, as an alternative to vanadium (II/III) redox couple. We identify two low-cost, aqueous based redox couples for spontaneous hydrogen generation on catalysts, 7,8-dihydroxyphenazine-2-sulfonic acid (DHPS) and ethylenediaminetetraacetic acid chelated chromium (Cr-EDTA) with ammonia. Hydrogen evolution rate of Cr-EDTA are two times higher than that of DHPS on Pt/C catalysts, but lower than a strong acid vanadium solution. Cr-EDTA solution has near neutral pH and DHPS solution has pH 14, enabling use of low-cost materials including stainless steel and non-PGM catalysts for hybrid flow cells as well as catalytic reactors, while the strong acid vanadium solution limits materials to corrosion resistant materials such as carbon-based materials for flow cells, costly superalloys like Inconel or Hastelloy for catalytic reactors. Flow cell with the Cr-EDTA with ammonia solution paired with Fe(CN)6^{-4/-3} redox couple near neutral pH demonstrates coulombic efficiency of 99% with negligible hydrogen evolution side reaction. Cr-EDTA with ammonia is the first use for flow batteries to the best of our knowledge and seems very promising for spontaneous hydrogen generation as well as a negolyte for flow batteries.

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1.0 Introduction

Low-cost hydrogen using renewables will be a key enabling technology in the power-to-gasto-power (PGP) systems as well as in the GW scale and affordable long-term grid storage technologies. However, current multi-stage mechanical compression from 30 bar to 700 bar costs a lot (\sim \$1.54/kg-H₂)¹. As an ARPA-E open innovation, PNNL and Caltech have successfully demonstrated simultaneous generation and compression of hydrogen (350 bar) in a chemical catalytic reactor using an acid vanadium solution, in which V(II) will be oxidized to V(III) while proton will be reduced to hydrogen. The simple technoeconomic analysis shows the hydrogen compression cost is $0.35/kg-H_2$ and the entire system cost is projected to be < $4/kg-H_2$. comparable or lower than the corresponding cost for existing PEM electrolysis, which is still higher than the widespread deployment cost goal (< \$2/kg-H₂)². One contribution to high cost comes from expensive vanadium as a redox mediator. In our work, to further reduce the cost, we looked for vanadium-alternative, low-cost aqueous redox molecules as a proton source. Furthermore, we investigated the mild acid, neutral or alkaline media as a supporting electrolyte to enable more flexible material selection in the catalytic reactor design and low-cost hydrogen evolution catalysts. These efforts will help to advance the scientific knowledge in this exploratory research and decarbonize the world.

2.0 Screening redox couples for spontaneous H2 evolution

To screen candidates of redox couples which can generate hydrogen spontaneously on catalysts, the half-cell potential of the candidate redox couple is required to be lower than the reversible hydrogen electrode (RHE) potential under operating conditions. Moreover, we excluded redox couples operating under strong acidic environments requiring expensive corrosion-resistant superalloys for a catalytic reactor system, while we considered redox couples operating under mild acid, neutral and alkaline aqueous solutions. Half-cell potentials of candidate redox couples used as a negolyte for aqueous flow batteries are summarized in Table 1. Among them, viologen, anthraquinone and fluorenone are dropped because the reported half-cell potential is higher than RHE, indicating energy is required for hydrogen evolution. Phenazine derivatives, 7,8-dihydroxyphenazine-2-sulfonic acid (DHPS) and 2,3-dihydroxyphenazine (DHP) are reported to have a similar or lower half-cell potential in alkaline solution ³, and chelated chromium with ethylenediaminetetraacetic acid (EDTA) is also reported to shift the $Cr^{2+/3+}$ half-cell potential from -0.41 to -0.99V vs. SHE near neutral pH ⁴. Here, we explored feasibility of DHPS, DHP, and Cr-EDAT redox couples as a spontaneous hydrogen evolution candidate.

Redox couples	рН	E _{-half cell} (vs. SHE)	Note
Viologen	~7	- 0.388 ~ - 0.368	E > RHE (-0.413 V vs. SHE)
Anthraquinone	~14	- 0.62	
Fluorenone	~ 14	- 0.69	E > RHE (-0.020 V VS. SHE)
DHPS	~ 14	- 0.93	E < RHE (-0.828 V vs. SHE)
DHP	~ 14	- 0.83	$E \approx RHE$ (-0.828 V vs. SHE)
Cr-EDTA	~7	- 0.99	E < RHE (-0.828 V vs. SHE)

Table 1. Half-cell potential of redox couples at operating pH

To validate the half-cell redox potential of Cr-EDTA and onset potential of hydrogen evolution on Pt/C catalysts, cyclic voltammetry tests were conducted using 0.5 M Cr(III)-EDTA solution for a Vulcan XC 72 carbon black powder-coated glassy carbon working electrode and a Pt/C catalyst-coated working electrode (Figure 1). The redox potential of Cr(II)/Cr(III) in the Cr-EDTA solution with pH=9 was observed at approximately -0.57 V vs. RHE (-1.08 V vs. SHE), while the onset potential of hydrogen evolution at the same pH on the Pt/C catalysts was observed at approximately -0.2 V vs. RHE. It indicates that hydrogen can evolve spontaneously on catalysts in the Cr-EDTA solution. Note that thermodynamic potential of Cr-EDTA for hydrogen evolution is higher than that of V (-0.55 V vs. -0.22 V).





Figure 1 compared cumulative hydrogen evolution with time on Pt/C catalysts of DHPS and Cr-EDTA redox couples, and rates are summarized in Table 2. Hydrogen evolution was observed in the reduced DHPS (noted as DHPS-2H) and Cr-EDTA solutions, but it was not observed in the reduced DHP solution which has a negligible thermodynamic driving force. Hydrogen amount evolved in the electrolyte solution increases with time, but its rate gradually decreases, eventually to zero because the reduced active species concentration decreases with time. Hydrogen evolution rate is the fastest in the acidic vanadium solution, the next in the near neutral Cr-EDTA, and the slowest in the alkaline DHPS electrolyte. This rate difference can be induced by reaction differences: in the acidic vanadium solution hydrogen gas is a product of chemical reduction of two protons (Eq 7, 8 and 9) while in the neutral and alkaline solutions hydrogen gas is produced by water decomposition (Eq 3 and 6). The fully reduced active species in vanadium and Cr-EDTA electrolytes is almost converted to hydrogen gas, but approximately 50% of the fully reduced DHPS is converted to hydrogen gas. It may be related with thermodynamic driving force differences. The thermodynamic potential of Cr-EDTA is 0.55 V, 5 times higher than that of DHPS (0.1 V). The Cr-EDTA has approximately two times higher thermodynamic potential, but its slower rate of hydrogen generation may be more complex reaction in the neutral solution. Hydrogen

(9)

evolution of charged DHPS is not sensitive to pH (Figure 2 and Table 2) because decreased pH increases half-cell reversible potential of DHPS as well as RHE, but the difference between DHPS and RHE is not changed. Note that hydrogen evolution was in the static conditions, and its rate can be enhanced with stirring or flowing conditions.

Alkaline or neutral

$\text{DHPS} - 2\text{H} + 2\text{OH}^- \rightarrow \text{DHPS} + 2\text{H}_2\text{O} + 2\text{e}$	$E^{rev} = -0.10V \text{ vs RHE (pH 14)}$	(1)
$2Cr(II) - EDTA(aq) \rightarrow 2Cr(III) - EDTA(aq) + 2e$	$E^{rev} = -0.55V \text{ vs RHE (pH 9)}$	(2)
$2\mathrm{H}_2\mathrm{O} + 2\mathrm{e} \rightarrow \mathrm{H}_2 + 2\mathrm{OH}^-$	$E^{rev} = 0.0V vs RHE$	(3)

$$DHPS - 2H(aq) \rightarrow DHPS(aq) + H_2(g)$$
(4)

$$2Cr(II) - EDTA(aq) + 2H_2O \rightarrow 2Cr(III) - EDTA(aq) + H_2(g) + 2OH^-$$
(6)

Acid

$2V(II)(aq) \rightarrow 2V(III) + 2e$	$E^{rev} = -0.26V \text{ vs RHE}$	(7)
$2H^+ + 2e \rightarrow H_2(g)$	$E^{rev} = 0.0V vs RHE$	(8)

$2V(II)(aq) + 2H^+ \rightarrow 2V(III) + H_2(g)$

Figure 2. Accumulated amounts of hydrogen per molarity of redox couples with time (min) for charged redox couples on the Pt/C coated carbon cloth electrode. Pt/C coated carbon cloth electrode was fully submerged in a 15 mL centrifuge tube, where 6mL of 1 M V(II), 6 mL of 1M DHPS-2H and 12 mL of 0.5M Cr(II)-EDTA is used respectively for each test.

Redox couples	рН	Hydrogen evolution rate (mL/M·hr)	SOC t=0	Theoretical max H2 volume (mL) @ 25 °C	Charged amount (Ah)
1 M V(II)	< 0	68.5	< 99	~74	
1 M DHPS	~ 14	25.7	< 99	~148	0.2936
1 M DHPS	~ 12	24.3	< 99	~148	0.2887
1 M DHP	~ 14	0	< 99	~ 148	-
0.5 M Cr-EDTA	9	44	< 90	~67	0.1510

Table 2. Comparison of spontaneous hydrogen evolution of various redox couples.

Note that initial SOC is estimated based on actual charged amount divided by theoretical capacity. Almost charged vanadium and Cr-EDTA molecules are discharged to generate hydrogen gas, but ~ 50% of DHPS is discharged for H2 generation. Hydrogen evolution rate was calculated by total hydrogen volume collected for initial one hour divided by concentration.

Compared to the vanadium redox couple, Cr-EDTA has its benefits as an alternative electron mediator for the hydrogen evolution. Most of all, we can bring down material cost from cheaper raw material cost of chromium ^{5,6} and commercially available EDTA ligands with competitive prices with its large market size compared to other metal chelating ligands. The ferrovanadium (FeV80, 80% V) is \$24.8/kg⁷ but average price of ferro-chrome (> 65% Cr, < 0.1% C) is US\$3.27/kg⁸ and price of chrome metal (> 99% Cr) is US\$9.1/kg⁹.

Additionally, vanadium redox couple in strong acid (pH < 0) requires corrosion resistant materials, typically limiting carbon-based materials and PVC plastics in FB system. Especially in the high-pressure (up to 700 bar) catalytic reactor system, the materials for reactor system build are limited to high-cost superalloys like Inconel or Hastelloy. By changing strong acid media to mild acid, near neutral or alkaline, low-cost materials like stainless steel can be used for high-pressure catalytic system, leading to significant cost reduction of the system. Mild acid, near neutral or alkaline media also enable use of low-cost non-PGM catalysts for hydrogen evolution, which has various opportunities of further cost reduction.

3.0 Flow battery performance

In addition to spontaneous hydrogen generation of DHPS and Cr-EDTA, the redox couples serve as negolyte for flow batteries. Flow cell characteristics of the DHPS redox couple are well described in literature ³. Cr-EDTA complex was first reported by Hamm in 1953 ¹⁰ but there was no significant studies on the complex as a redox couple till Roberts et al. ¹¹ explored it in a mild acid media. Later, Marshak et al. ¹² introduced Cr-PDTA (propylenediaminetertaacetic acid) chelate with near neutral pH as a negolyte of aqueous flow battery, enabling highly negative half-cell potentials (- 1.09V vs. - 0.41V vs. SHE for Cr²⁺/Cr³⁺) while inhibiting hydrogen evolution side reaction. They also compared the flow cell performance with Cr-EDTA and Cr-PDTA as a negolyte each paired with Fe(CN)₆ redox couple as a posolyte. Coulombic efficiency of the flow cell with Cr-PDTA is 99.5% while that of Cr-EDTA is 88% indicating significant hydrogen evolution ¹². They adjusted pH 9 using potassium tetraborate (KBi).

Interestingly, our Cr-EDTA with ammonium hydroxide as a buffer solution to adjust pH 9 was observed to inhibit hydrogen evolution side reaction effectively. Figure 3 shows the flow cell can be operated very stably, and its coulombic efficiency is 99%, indicating negligible hydrogen evolution side reaction.



Figure 3. Flow battery cycling performance with a 10 cm2 active area, where a 10 mL negolyte of 0.6 M Cr-EDTA + 0.2 M KCl and a 30 mL posolyte of 0.4 M Na4Fe(CN)6 + 0.2 M K3Fe(CN)6 + 0.2 M KCl are used. The negoylte pH was adjusted to 9 by ammonium hydroxide solution.

Ammonia is typically used as a complex agent in the aqueous solution. Chromium (III) ions in aqueous solution exists in the hydrated form, hexaaquachromium(III) ion, $[Cr(H_2O)_6]^{3+}$. If ammonia solution is added to the solution, ammonia replaces hydrated water molecules as a ligand to give hexaamminechromium(III) ions, $[Cr(NH_3)_6]^{3+13}$. Marshak et al. ¹² hypothesized that the coordination of water molecule to Cr-EDTA, $[Cr(EDTA)(H_2O)]^{3+}$ may facilitate water splitting, while Cr-PDTA excludes water from the primary coordination sphere, inhibiting hydrogen evolution side reaction. In a similar way, we hypothesize that ammonia replaces water molecule in $[Cr(EDTA)(H_2O)]^{3+}$ and forms $[Cr(EDTA)(NH_3)]^{3+}$, which helps inhibit hydrogen evolution side reaction. Cr-EDTA with ammonia is the first use for flow batteries to the best of our knowledge and seems very promising for spontaneous hydrogen generation as well as a negolyte for flow batteries. Further research on understanding of molecular structures, optimized composition and various ligands are required.

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Appendix A – Methodology

1. Chemicals

Chromium (III) Chloride Hexahydrate; Ethylenediaminetetraacetic acid, ammonium hydroxide solution (65~70%), 7,8-dihydroxyphenazine-2-sulfonic acid (DHPS), sodium hydroxide, potassium ferrocyanide. Vanadyl (IV) sulfate, and sulfuric acid.

2. Test methods

• Cyclic voltammogram

The three-electrode configuration was set up for the CV test. A graphite rod, a mercury sulfate and saturated potassium sulfate reference electrode, and a Vulcan XC 72 carbon black powder coated glassy carbon electrode were used as the counter, reference, and working electrodes, respectively. For the hydrogen evolution reaction test, 10 μ L of 5 mg/L Pt/C catalyst ink was drop-coated onto the glassy carbon electrode. The scan rate is 50 mV/s, and the electrolyte is a 0.1 M Cr-EDTA solution with a pH of approximately 9.

• Measurement of hydrogen evolution rate

Before measuring the hydrogen evolution of DHPS, Cr-EDTA, and DHP redox couples on Pt/C catalysts, the reduced electrolyte of each was prepared by electrochemically charging a flow cell with paired with a $Fe(CN)_6^{3-/4-}$ redox couple. The same flow cell configuration as described in below section of flow battery test was used. Each solution was placed in a centrifuge tube where 6 mL of 1 M DHPS-2H (aq), 6mL of 1 M V(II) (aq), 6mL of 1 M DHP-2H (aq), and 12 mL of 0.5 M Cr(II)-EDTA (aq) were used. Then, 2 × 5 cm² of Pt/C coated carbon electrode was fully submerged into the electrolyte and the tube was closed with a lined stopper to allow generated gas to flow into a burette filled with water. The collected gas volume was monitored until the generation rate is less than 1 mL/hr.

• Flow battery test

Cr(III)-EDTA solution was prepared by a following method. The chromium (III) chloride (21.3 g, 80 mmol) and EDTA (26.3 g, 90 mmol) were dissolved in 30 mL of DI water and heated to 110 °C. After 1 h of heating, 10 g of potassium hydroxide was added slowly at 110 °C. After 24 h, 16 mL of 5 M KOH solution was added. Another 16 mL of 5 M KOH was added after addition 24 h of heating. The solution is finally cooled to room temperature, and then filtered through a filter paper to get rid of remaining EDTA. The pH of the prepared solution was less than 5, and then was adjusted to 9~10 by adding a couple of drops of ammonium hydroxide solution. KCI is added to the prepared solution to increase the conductivity. The final composition of the negolyte is 0.6 M Cr-EDTA + 0.2 M KCI. The posolyte was prepared with 0.3 M sodium ferrocyanide, 0.1 M potassium ferricyanide, and 0.2 M KCI supporting electrolyte in 45 mL of DI water and the pH is adjusted with ammonium hydroxide solution. The flow cell used an interdigitated design of an active area of 10cm2 (2cm * 5cm) with stacked layers of two carbon papers (Freudenberg HC23) and one Elat carbon cloth electrodes sandwiching Nafion 212 membrane. The negolyte and posolyte volumes are 10mL and 35 mL respectively, and the flow rate is 40mL/min and current density is 50 mA/cm².

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