A Stand-Alone Module for Solar-Driven H₂ Production Coupled with Redox-Mediated Sulfide Remediation

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Abstract

Efficient electrochemical devices are required to convert electric power generated by intermittent renewable energy sources into a chemical form. Among the electrochemical methods considered, the choice of combination in reduction-oxidation reactions can vary depending on the target, which provides different thermodynamics and kinetics. A promising approach for H₂ production coupled with sulfide remediation is demonstrated to utilize intermediate redox media. H₂ is produced on the cathode, and soluble redox ions in a reduced form are oxidized on the anode. The ions are then transferred to a separate reactor to oxidize the sulfide ions via a homogeneous reaction, and the reduced redox ions are recirculated. A

solar-driven redox photovoltaic-electrochemical (PV-EC) system is operated as a stand-alone module and is composed of Cu(In,Ga)(S,Se)₂ (CIGS) photovoltaics and electrochemical cells in series and operated under natural solar irradiation. A unique electrochemical cell is established in an aqueous-phase membrane-less configuration at ambient temperature, and a cathode is decorated with a semipermeable CrO_x-based nano-membrane. This allows for selective H₂ evolution without causing Fe-redox reduction. Remaining issues associated with the stability of the CrO_x permselective layer on the cathode are also discussed, which are associated with the formation constant of a soluble metal complex in the presence of ligand counterions.

1. Introduction

During the last few decades, there is a growing interest globally for renewable energy sources, such as solar energy and wind power. Their intermittent nature, however, prevents a massive introduction of renewable based electricity to the existing electricity grids and limits their application. Therefore electrochemical energy conversion and storage technologies are required. Tremendous efforts have been devoted to developing solar-driven water-splitting devices (**Equation 1**) using light-absorbing semiconductors and electrocatalysts in aqueous solution.

The overall voltage for a water-splitting device is determined by its thermodynamics (1.23 V), Ohmic losses, concentration overpotential, which comes from the concentration gradient between the bulk solution and the electrode surface, and kinetic overpotentials on the electrocatalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Particularly, OER requires large overpotential of more than 200 mV at 10 mA cm⁻² in highly alkaline conditions with finely tuned electrocatalysts on a support with high surface area.^[1–3]

The anodic reactions to produce hydrogen on a cathode are not limited to OER. For instance, chlorine evolves from chloride ion on an anode while HER takes place on a cathode in a commercialized chloro-alkaline process.^[4] Alternative oxidation reactions have been proposed to replace the kinetically sluggish OER to the production of valuable chemicals, such as oxidative upgrading of biomass feedstock and the production of oxidizing agents like hydrogen peroxide and peroxydisulfate anions.^[5–10] Another promising anodic reaction during HER (**Equation 2**) involves oxidizing soluble redox ions (**Equation 3**), which can perform a subsequent homogeneous reaction, such as the oxidation of toxic H₂S into solid sulfur.

Ox and Red denote the oxidized and reduced redox species, respectively. The oxidized redox ions oxidize S₂²⁻ in the subsequent homogeneous reaction (**Equation 4**).

Combining Equations 2-4, the overall reaction involves splitting H₂S into H₂ and S (**Equation 5**), while redox ions serve as charge carriers between the anode and sulfide; that is, redox-mediated H₂S splitting.

The advantage of this approach is that valuable H₂ is regenerated from H₂S while conventional H₂S treatment processes such as the Claus, LO-CAT, and Sulferox processes oxidize H₂S into H₂O and S using O₂ (**Equation 6**).^[11,12]

Water splitting requires more than 1.23 V, which means that 3 Si photovoltaic (PV) cells in series are necessary to obtain a sufficient voltage for solar-driven H₂ production because one Si-PV has merely 0.6 V as its open circuit voltage.^[13] The advantage of H₂S splitting is that it thermodynamically requires 0.14 V, which provides a variety of options to combine PVs and electrochemical (EC) cells.

Although direct electrochemical H₂S splitting, in which an anode directly oxidizes sulfide to solid sulfur, can be performed theoretically, the deposition of solid sulfur on the anode is a challenge to be overcome.^[14,15] The redox-mediated H₂S splitting process requires no passivation of electrodes because the sulfur precipitation takes place through a homogeneous reaction outside the EC cell. Separation and purification process of the sulfur product has been well established in the commercialized liquid phase processes for H₂S treatment, such as LO-CAT and Sulferox, in which reduced redox ions after reaction with sulfide are reoxidized by bubbling O₂. A variety of redox ions have been investigated for redox-mediated H₂S splitting, such as Fe-based redox, iodide, vanadate, and heteropoly molybdo-phosphate.^[16–21] A previous study investigated candidate redox ions in buffered near-neutral pH condition, particularly Fe-based metal complexes.^[22] Near-neutral pH conditions were chosen because there are optimal potential options for using non-noble metal cathodes, whereas acidic conditions require noble metal cathodes. In that study, Fe_{2+/3+}-hydroxyethylethylenediaminetriacetate (HEDTA) was identified as a suitable candidate due to its redox potential (0.43 V vs. reversible hydrogen electrode (RHE) at pH 3–8; **Figure S1**) and its remarkable solubility (> 1 mol kg^{−1}). The redox potential of Fe_{2+/3+}-HEDTA is close to the potential to oxidize sulfide to sulfur (0.14 V vs. RHE) compared with other Fe candidates. The remarkable solubility should also help to increase the diffusion flux of the redox ion.

There are a few approaches to combine light-absorbing semiconductors and electrodes to perform solar-driven H₂ production. Photoelectrochemical and photocatalytic approaches involve immersing the semiconductors in the electrolyte, and electrochemical reactions take place on the surface of semiconductors or electrocatalysts that are deposited on the semiconductors. A solar-to-hydrogen (STH) conversion efficiency of 16% has been reported for water splitting,^[23] but the stability of semiconductors in electrolyte remains a major challenge. Redox ions can absorb visible light and compete with the semiconductor, so these approaches are not suitable for the present application. Isolating semiconductors from the

electrolyte is a reasonable approach in terms of stability and light management. Commercially available PVs can be readily employed with EC cells via direct connection^[13,24–27] or through power electronic devices such as DC-DC convertors.^[28–30] A DC-DC convertor with maximum power point tracker (MPPT) helps to transfer the maximum power of the PV module to the EC module, but it requires additional investment costs. On the other hand, the current and voltage have to be carefully matched between the PV module and EC module by varying their size and the number of EC cells within the module in the case of direct connections without a DC-DC convertor. A synergetic effect is expected when PV module is directly integrated on top of EC module. The efficiency of the PV module decreases at elevated temperature under light irradiation. Therefore, in the integrated device, the electrolyte is expected to cool down the PV module, while the heat transferred from the PV module to the electrolyte improves the electrochemical reaction kinetics, mass-transport, and conductivity during electrochemical reactions.^[31–34]

In this study, a stand-alone module was produced by directly connecting Cu(In,Ga)(Se,S)₂-PV (CIGS-PV, irradiation area: 168 cm²) module and EC module in series. The module is used to produce H₂ coupled with the oxidation of Fe²⁺-HEDTA redox under natural light irradiation for subsequent sulfide treatment (**Figure 1**) in which Na₂S solution is introduced as a model sulfide source instead of H₂S gas due to the safety concern. Hydrogen is the only gaseous product from the electrochemical system, while hydrogen and oxygen are produced in water splitting devices, which require an ion exchange membrane or a diaphragm between the anolyte and the catholyte to separate the gases produced. A crossover could take place on the cathode, where oxidized Fe³⁺-HEDTA ion can be reduced instead of HER. To avoid the crossover, a nano-membrane coating was applied on the HER catalyst (bottom image in Figure 1), which prevents the diffusion of large redox ions to reach the electrocatalyst underneath while allowing protons and hydrogen to go through.^[35–42] In this work, CrO_x was employed as a model nano-membrane layer for the ion exchange membrane free device because

of its well known functionality for corrosion protection, photocatalytic water splitting and electrochemical chlorate production.[35–37,43,44] The applicability of CrO_x for the present application is also discussed.

2. Results and Discussion

2.1. Evaluation of Individual Electrochemical Cell Performance

To evaluate the EC cell, electrochemical measurements were performed with 1.0 mol kg^{-1} of Fe-HEDTA (50 % Fe^{2+} and 50 % Fe^{3+}) and 1.5 mol kg^{-1} of malonate buffer (pH = 5) using a carbon felt anode and a CrO_x/Pt -black mesh (geometric area: $1 \times 1 \text{ cm}^2$) under static conditions at room temperature (**Figure 2a**). The onset potential appears at approximately 0.41 V, which agrees with a previous report.[22] The current density monotonically increases when applying a positive voltage between the anode and cathode.

A three-electrode configuration was used to measure the potential of electrodes from a reference electrode and the resistance between the anode and cathode, which can be used to evaluate the individual overpotentials for the HER, redox oxidation, and Ohmic loss. A current density of 10 mA cm^{-2} was achieved within 100 mV of overvoltage to oxidize the redox ion with an ubiquitous carbon felt anode in a static condition, whereas the kinetically sluggish anodic OER requires more than 200 mV with finely tuned electrocatalysts.[1–3] This confirms that the oxidation of Fe^{2+} -HEDTA is a promising alternative anodic reaction to minimize the kinetic contribution. In general, the overpotential on electrodes derives from two contributions, namely kinetic overpotential and concentration overpotential. The kinetic overpotential comes from an intrinsic heterogeneous electron transfer kinetics of the electrode alone while the concentration overpotential arises from an unavoidable concentration gradient due to the mass-transport between the bulk solution and the electrode surface during reaction. Identifying their contributions is essential to determine the direction to reduce overpotential either by the development of electrode material to improve kinetics or by engineering surrounding

electrolyte and reaction condition, such as stirring and operating temperature, to enhance mass-transport. In a previous study, a quantitative approach using a glassy carbon rotating disk electrode (RDE), which produces a well defined vigorous convection, revealed that the majority of the overpotential observed for the present redox ions comes from mass-transport limitation.^[22] Because the measurement with the carbon felt in Figure 2a is performed in the static condition, the observed overpotential has even severe mass-transport limitation compared with that in the RDE configuration performed in the previous study. Thus, the overpotential in the present system could be reduced by improving the mass-transport through methods such as convection and elevating the temperature. The j - V curve was measured as a reference using a glassy carbon RDE at 900 rpm in a solution containing 1.0 mol kg⁻¹ of Fe_{aq}2+/3+ in 0.5 mol L⁻¹ of H₂SO₄. To obtain the solution for Fe_{aq}2+/3+ acidic pH was chosen to maintain Fe_{aq}2+/3+ ions in the absence of ligands, whereas the solution for Fe_{2+/3+}-HEDTA was near-neutral pH buffered condition (pH = 5). The onset potential appeared around 0.7 V vs. RHE, which is more positive than that of Fe-HEDTA. This result indicates that the redox potential of Fe_{aq}2+/3+ was successfully tuned by the formation of a metal complex, which helps to reduce the voltage for EC cell to perform the HER and the oxidation of redox ions.

The overpotential for HER to reach 10 mA cm⁻² is approximately 150 mV on a CrO_x/Pt mesh in the present redox solution. This value is larger than that reported for NiMo/Ni-foam (30 mV) in phosphate buffer without redox ions, which is a standard solution for water splitting in near-neutral pH conditions.^[45] HER on Pt is known to be kinetically facile, and the observed overpotential is mainly due to the concentration overpotential from proton donors and hydrogen products.^[45–47] The concentration overpotential is highly dependent on the viscosity of the electrolyte, which alters the diffusion coefficient according to the Stokes-Einstein equation. Diffusion coefficient decreases in viscous solutions, which makes the mass-transport of reactants and products difficult and results in the increase of concentration overpotential. The viscosity of the present dense redox solution is approximately 3 mPa s, while that of the

phosphate buffer solution optimized for HER ($0.5 \text{ mol L}^{-1} \text{ K}_{1.5}\text{H}_{1.5}\text{PO}_4$) is 1 mPa s . Since the present measurements were performed in static conditions at room temperature, improving the mass-transport by convection or elevated temperature is also expected to decrease the overpotentials on both the anode and the cathode.

In addition to the overpotential on the anode and cathode, the Ohmic loss needs to be considered. The conductance of the redox solution was 0.075 S cm^{-1} , which led an Ohmic loss of 90 mV at 10 mA cm^{-2} with a distance of approximately 5 mm between the anode and cathode. The Ohmic loss is comparable to the kinetic losses on the anode and the cathode, so design optimization for the EC cell is required to minimize the distance between the anode and the cathode. Overall, a steady-state operation at $10 \text{ mA cm}^{-2}_{\text{geo}}$ was achieved within 0.8 V to perform HER and the oxidation of redox ions, which is smaller than the voltages of 1.4 V and 1.6 V for water splitting with a polymer electrode membrane and an alkaline electrolyzer, respectively.^[24,27]

The I - V curve for a CIGS-PV module that contains 14 PV cells in series was measured under simulated solar conditions (air mass (AM) 1.5G), as shown in **Figure 2b**. The solar-to-electricity (STE) conversion energy efficiency was 15.5% with a fill factor of 68.3%. The voltage at the maximum power of the CIGS-PV module is 7.6 V , and the EC cell requires 0.8 V to reach $10 \text{ mA cm}^{-2}_{\text{geo}}$. Therefore, nine EC cells in series with 40 cm^2 electrode area in the individual cells are suitable to transfer the power generated from the PV cell effectively.

2.2. Solar-Driven Hydrogen Evolution Demonstration Coupled with Oxidation of Fe^{2+} -HEDTA

An EC module was designed with six EC cells (**Figure 3a**) to guarantee operation with the CIGS-PV module. Carbon felt was used as the anode ($1.8 \times 22.5 \text{ cm}^2$, 3 mm thickness, **Figure 3b**). Pt was sputtered on SUS mesh (Pt/SUS mesh, $1.8 \times 22.5 \text{ cm}^2$) (**Figure 3c**), and six sheets of the Pt/SUS mesh were put together to obtain a sufficient surface area of Pt. The Pt/SUS

mesh and carbon felt were connected in series with Teflon-coated copper wires. A spacer with a thickness of about 2 mm was used to prevent a short circuit between the anode and cathodes (**Figure 3d**).

A stand-alone module was assembled as shown in **Figure 3e and 3f** and used to produce H₂ gas, which was collected in a graduated cylinder. To obtain *I-V* curve of the PV module under natural sunlight, one of the CIGS-PV module was used as a reference and connected to a potentiostat. Although PV-EC modules were placed beside each other to observe the electrochemical reactions in this demonstration, a compact stand-alone module can be fabricated just by placing the PV module on top of the EC module (**Figure 3g**).

The light intensity was measured using a Si photodiode as approximately 100 mW cm⁻², which was close to the standard intensity of AM 1.5G during a demonstration on December 6, 2018, in Thuwal, Saudi Arabia. The current through the system was monitored using a multi-meter connected in series (**Figure 4a**). During the initial 10 min of experiment, increasing current was observed from 250 to 320 mA. The activation might come from the initial conditioning of electrodes by redox reactions or a slight elevation in the temperature of the electrolyte by solar irradiation. After this induction period, a stable current of approximately 330 mA was obtained during the demonstration, which corresponds to 8 mA cm_{geo}⁻² based on the electrode area (40.5 cm²) in the individual cells.

Hydrogen gas bubbles were successfully observed from the cathodes in all EC cells (**Supporting movie 1**), and the production rate was approximately 15 mL min⁻¹ (0.61 mmol min⁻¹) from 168 cm⁻² of PV module (**Supporting movie 2**). This corresponds to 0.09 mL cm⁻² min⁻¹ (222 μmol h⁻¹ cm⁻²). Faradaic efficiency determines the percentage of current used for a desired reaction which HER on the cathode. Comparing the volume of the hydrogen collected in the cylinder and theoretical one estimated from the measured current, nearly 100% Faradaic efficiency was obtained at the beginning of the measurement (**Figure 4a**). Potential side reactions on the anode were examined for oxidation of the malonate buffer and H₂ on a glassy

carbon rotating disk electrode, and the results are shown in **Figure S2**. Negligible current was obtained in the absence of $\text{Fe}_{2+/3+}$ -HEDTA redox ion, or in the presence of H_2 , which supports that the anodic current in the stand-alone module comes merely from the oxidation of Fe_{2+} -HEDTA redox ion.

The *I-V* results of the reference PV showed 12% STE conversion energy efficiency under natural solar irradiation and was compared with the voltage of individual EC cells measured by a multi-meter connected in parallel (**Figure 4b**). The voltage of individual EC cells was approximately 0.7-0.9 V, which is consistent with the measurement obtained using a $1 \times 1\text{-cm}^2$ geometry in the laboratory shown in Figure 2a, except for the EC cell No. 3, which required 1.3 V. This was later found to be the result of a loose connection between the electrode mesh and copper wire in this EC cell.

The overall voltage for the EC module was 5.1 V. The current at 5.1 V in the reference PV module was 330 mA, which is consistent with the measured current of the stand-alone module. Figure 4b clearly shows that the stand-alone device was operated at a voltage below the maximum power of the PV cell ($V_{\text{Pmax}} = 6.5\text{ V}$), where stable current can be obtained, while the current is expected to drop significantly above V_{Pmax} . However, the Faradaic efficiency gradually kept dropping to 80% after 60 min, which indicates the presence of a side reaction with Fe_{3+} -HEDTA on the cathode (Figure 4a). The stability of the CrO_x layer in the presence of redox ions is further discussed in section 2.4.

The various efficiency results are summarized in **Table 1**. The efficiency of the PV-to-EC power transfer (the power utilization) was 85% according to the operating point and maximum power of the PV cells. The PV-to-EC power transfer efficiency is expected to be improved further by increasing the number of EC cells based on V_{Pmax} of the PV module and the operation voltage of individual EC cells. The STH conversion energy efficiency can be evaluated with a variety of thermodynamic voltages, which depend on the counter half reaction.

The counter half reaction is denoted in parentheses to describe the corresponding STH conversion energy efficiency.

Table 1. Various efficiencies for the stand-alone device measured at 2:10 pm on December 6, 2018, in Thuwal, Saudi Arabia.

Term	Definition	Efficiency / %
Solar-to-electricity (STE) conversion energy efficiency	$\frac{\text{Power max of PV}}{\text{Input light intensity}}$	12
PV-to-EC power transfer efficiency	$\frac{\text{Power at operation}}{\text{Power max of PV}}$	85
Solar-to-hydrogen (STH) conversion energy efficiency (S_2/S)	$\frac{\text{Production rate of } H_2 \times 2 \times 0.14}{\text{Input light intensity}}$	1.4
Solar-to-hydrogen (STH) conversion energy efficiency (Red/Ox)	$\frac{\text{Production rate of } H_2 \times 2 \times 0.43}{\text{Input light intensity}}$	4.4
Voltage efficiency for the electrochemical system	$\frac{0.43 \times 6}{\text{Operating voltage}}$	51

The STH conversion energy efficiency for H_2S into H_2 and S uses the thermodynamic voltage of 0.14 V (third row in Table 1). The STH conversion energy efficiency (S_2/S) was 1.4%, which represents the net efficiency for the solar-driven H_2 production coupled with sulfide remediation shown in Figure 1. The STH conversion energy efficiency (Red/Ox) was 4.4% when introducing the thermodynamics of redox ions, which represents the efficiency of the present stand-alone device only without considering the homogeneous reaction with sulfide. Voltage efficiency discusses the energy loss due to the overpotentials in the electrochemical cells during operation compared with the thermodynamics of the desired reaction. The voltage efficiency for the electrochemical module was 51% from the operating voltage (5.1 V) and the thermodynamically required voltage for HER and the oxidation of redox ions ($0.43 \text{ V} \times 6 \text{ EC cells}$). The voltage efficiency for water splitting is reported to be 70-80% in alkaline electrolyzers and 95% in polymer electrolyte membrane (PEM) electrolyzers, even at high current density (200 mA cm^{-2}).^[48] Although the sluggish OER was replaced with the kinetically facile redox reaction, there is a large voltage loss in the present system compared with a water-splitting device. One of the reasons is the thermodynamic voltage. The water splitting

thermodynamically requires a large voltage (1.23 V), so the portion of additional losses (Ohmic drop and the overpotentials on anode and cathode) appears to be smaller than in the present reaction, which requires 0.43 V.

Solar-to-hydrogen conversion energy efficiency 10% is often used as a benchmark for solar-driven water splitting, which corresponds to the H_2 production rate $153 \mu\text{mol cm}^{-2} \text{ h}^{-1}$. Although the energy efficiency to split H_2S is low in the present stand-alone module, the H_2 production rate was $222 \mu\text{mol cm}^{-2} \text{ h}^{-1}$, which exceeds the above-mentioned benchmark value for water splitting. Higher H_2 production rate can be easily obtained because the required voltage for the present reaction is significantly lower than that for the water splitting, which helps to increase the current density and resultant H_2 production rate per unit area.

The STH conversion energy efficiency could be improved further. For instance, the number of EC cells could be optimized according to the generated voltage of the PV, which would improve the PV-to-EC power transfer efficiency. The voltage efficiency could also be improved through fine tuning the electrolyte and elevating its temperature to decrease the additional voltage losses in the electrochemical module, especially the diffusion overpotential and Ohmic loss. Improvement is also necessary for the Faradaic efficiency of H_2 , which remained 80% after the gradual degradation of CrO_x nano-membrane layer. The origin of degradation and alternative candidates are discussed in section 2.4.

2.3. Homogeneous Reaction Between Fe^{3+} -HEDTA and S_2^{2-}

Instead of H_2S , $0.02 \text{ mol L}^{-1} \text{ Na}_2\text{S}$ solution was used as a model sulfide source. A stoichiometric volume of Na_2S solution was added to a $0.1 \text{ mol kg}^{-1} \text{ Fe}^{3+}$ -HEDTA solution with 1.0 mol kg^{-1} of malonate buffer, which has a red color, under Ar atmosphere at room temperature. The color of the solution turned to a deeper red immediately after the addition of the Na_2S solution and became opaque with the dispersion of particles (**Supporting movie 3**).

The following reaction mechanism between the H₂S and Fe-complex is suggested with **Equation 8** as a rate determining step.^[11]

The color changed to a deep red color because of the formation of a reaction intermediate in Equation 8, which has a light absorption peak at 490 nm.^[49] The reaction took a few minutes to complete at ambient temperature. In commercialized homogeneous processes to oxidize H₂S in liquid phase, such as the Lo-cat and Sulferox processes, the reaction temperature is elevated to 40-60 °C,^[11,50] which will help to increase the homogeneous reaction rate. The form of H₂S in the electrolyte depends on the solution pH. The major species is dissolved H₂S below pH 7, and it shift to HS⁻ up to pH 12, finally S₂⁻ in more alkaline conditions. Accordingly, concentration of dissolved sulfide species increases in alkaline condition. Although the major sulfide species is not clear when alkaline Na₂S solution was added to buffered redox solution (pH = 5) at this preliminary stage, homogeneous H₂S treatment to solid sulfur with redox ions is demonstrated in a wide pH range from highly acidic to slightly alkaline condition (pH = 9) in previous reports.^[11,16,18] Further study is required to optimize conditions, such as pH and temperature, for overall process including electrochemical systems and homogeneous reactors using H₂S gas as a sulfide source to achieve efficient solar conversion and H₂S treatment.

The precipitation was collected after centrifuging and washing with water. The Raman spectra confirmed that the powder obtained was composed of solid sulfur (**Figure 5a**). Characteristic peaks of Na₂S at 168 nm and 232 nm were not observed in the precipitate, which shows that sulfide ions reacted with Fe₃₊-HEDTA. The purity of the obtained solid sulfur is not studied at this preliminary stage because it highly depends on the washing and separation process. However, the commercialized Sulferox process which also applies Fe based redox

solution can produce 99.5% purity of sulfur after filtration and melting process.^[12] These existing techniques will definitely help the present redox-mediated process in the future work.

UV-vis spectra were collected with a series of redox solutions after diluting the concentration of Fe redox ions to 0.2 mmol L⁻¹ (**Figure 5b**). The Fe₃₊-HEDTA redox shows absorption below 450 nm with an absorption peak at around 250 nm, while the blank malonate buffer has absorption below 250 nm. A transparent supernatant was collected after the homogeneous reaction with sulfide and allowing it settle down overnight under Ar atmosphere (bottom inset photograph in Figure 5b). The absorption peak at 250 nm clearly decreased after reaction with Na₂S, which indicates that Fe₃₊-HEDTA was successfully reduced to Fe₂₊-HEDTA by the oxidation of sulfide ions. The absorption peak still remained, which might have come from unreacted Fe₃₊-HEDTA or the reoxidation of Fe₂₊-HEDTA by air during dilution. Characteristic peak of sulfide solution at 230 nm was not observed in the redox solutions after homogeneous reaction, which indicates that sulfide ions completely reacted with Fe₃₊-HEDTA redox ions. The collected transparent supernatant was subsequently stirred in the presence of air and returned to the original red color (top inset photograph in Figure 5b). The UV-vis spectra confirmed that Fe₂₊-HEDTA can be reoxidized to Fe₃₊-HEDTA, which indicates that the Fe_{2+/3+}-HEDTA redox ions can serve as reversible charge carriers. The cycle stability of the Fe_{2+/3+}-HEDTA redox ion during the electrochemical and homogeneous reactions for a longer duration should be investigated in the future for practical application. It is however considered that this present process only uses a mild anodic electrochemical potential (0.5 V vs. RHE according to Figure 2a) as opposed to the standard process using O₂ as a strong oxidizer,^[12] expecting a reasonable stability of Fe_{2+/3+}-HEDTA redox ion.

The presence of buffer ions is essential to minimize the concentration overpotential (pH gradient). The potential-pH diagram of various Fe-redox species shows that the oxidation of Fe-redox species requires an appropriate pH. For example, a dense Na₂S solution (1.0 mol L⁻¹) at highly alkaline pH failed to form solid sulfur as a black precipitation (**Figure S3**), resulting

in the formation of Fe_xS . In addition to the potential use of a non-noble metal cathode, near-neutral pH conditions in the presence of buffer (malonate in this case) offered an environment to make redox cycles achievable with the Fe-HEDTA redox solution.

2.4. Stability of the Permselective CrO_x Layer in the Presence of Metal Complex

A decrease in the Faradaic efficiency of H_2 was observed in the stand-alone device (Figure 4a). We postulated that the degradation of CrO_x layer came from an electrochemical reduction of solid Cr^{3+} containing layer to soluble Cr^{2+} ion during HER in the presence of metal complex. To confirm the hypothesis, electrochemical stability tests were performed with different oxidizers, i.e., O_2 , Fe^{3+} -HEDTA and $\text{Fe}(\text{CN})_6^{3-}$, and the potential-pH diagram was estimated in the presence of metal complexes.

The stability of the CrO_x layer was studied on a polycrystalline Pt RDE in the presence of O_2 , $\text{Fe}^{2+/3+}$ -HEDTA, or $\text{Fe}(\text{CN})_6^{4-/3-}$ by switching the electrode potential between HER (approximately -0.18 V vs. RHE) and 0 V vs. RHE at 1600 rpm. In the presence of O_2 , the measured current at 0 V vs. RHE remained close to 0 mA cm^{-2} during the stability test in 0.5 mol L^{-1} of phosphate buffer at pH 5 (**Figure 6a**). The diffusion-limiting current density for the oxygen reduction reaction (ORR) was approximately -5 mA cm^{-2} on a bare Pt electrode (**Figure 6d**). The suppression of ORR by the CrO_x layer is consistent with previous reports and is explained by the unique permselectivity through the layer.^[35–37] The CrO_x layer prevents the diffusion of O_2 while allowing the mass-transport of protons and H_2 . The cyclic voltammograms measured before and after the stability test remained unchanged (Figure 6d), which also indicate the excellent stability of CrO_x during HER in the presence of O_2 .

The stability test was also performed in the redox solution used for the demonstration, which contains 1 mol kg^{-1} of $\text{Fe}^{2+/3+}$ -HEDTA (50% Fe^{2+} and 50% Fe^{3+}). The measured current density at 0 V vs. RHE was close to 0 mA cm^{-2} at the beginning of the stability test, but it kept decreasing to approximately -4 mA cm^{-2} at the end of the potential-step stability test (**Figure**

6b). The current increase is ascribed to the reduction of Fe^{3+} -HEDTA, which has more positive redox potential (0.43 V vs. RHE). This suggests that the role of the permselectivity of CrO_x layer was not maintained.

In contrast, the current density remained 0 mA cm^{-2} when the stability test was conducted at a constant potential (0 V vs. RHE), which suggests that the semipermeable function of the CrO_x layer was gradually lost when applying more negative potential in the potential-step stability test. The cyclic voltammograms measured before and after the stability tests (**Figure 6e**) are also consistent with the chronoamperometry results. A reduction current was observed above 0 V vs. RHE, which originated from the reduction of Fe^{3+} -HEDTA after the potential-step stability test, while only HER current below 0 V vs. RHE was measured after applying constant potential (0 V vs. RHE). This loss of semipermeability of the CrO_x layer was very gradual because the reduction current measured at 0 V vs. RHE (-4 mA cm^{-2}) was smaller than that measured with a bare Pt electrode (-60 mA cm^{-2}).

To investigate the impact of a different metal complex, $\text{Fe}(\text{CN})_{64-3-}$ was introduced instead of $\text{Fe}^{2+/3+}$ -HEDTA to perform the stability test. Because of the limited solubility, the total concentration of $\text{Fe}(\text{CN})_{64-3-}$ was 0.5 mol kg^{-1} (50% Fe^{2+} and 50% Fe^{3+}). There was clearly severe decomposition of the CrO_x layer within 60 min (**Figure 6c**), although the concentration of redox ions was lower than that of Fe-HEDTA shown in Figure 6b. At the end of the stability test, the current density became close to the diffusion-limiting current density measured on the bare Pt (-110 mA cm^{-2}) shown in **Figure 6f**. Cyclic voltammogram of CrO_x/Pt after the stability test in Figure 6f shows the cathodic current coming from the reduction of $\text{Fe}(\text{CN})_{63-}$ above 0 V vs. RHE, which indicates that the functionality of CrO_x layer was lost.

The comparisons in Figures 6a-c imply that just the production of hydrogen gas (approximately -10 mA cm^{-2}) does not damage the CrO_x layer (Figure 6a) and that the degradation is influenced by the different type of Fe redox species (Figures 6b and c). Most critically, the degradation is highly dependent on the ligand of the redox species present in the

electrolyte. The comparison in Figure 6b indicates that applying a negative potential triggers the degradation, which implies that the potential dependent redox process is involved in the loss of the CrO_x layer.

The oxidation state of the CrO_x layer is supposed to be +3 after deposition, so the redox reaction from Cr^{3+} in CrO_x to soluble Cr^{2+} ions seems to be the origin of the degradation. To clarify this hypothesis, the thermodynamics of $\text{Cr}^{2+}/\text{CrO}_x$ was estimated in the presence of the metal complex. Although CrO_x layer is suggested to be mixed oxide and hydroxide $\text{CrO}_{(1.5-m)}(\text{OH})_{2m} \cdot y\text{H}_2\text{O}$,^[51,52] it is assumed that the CrO_x is $\text{Cr}(\text{OH})_3$. The activity of the solid phase is unity, and the total activity of Cr^{2+} ions ($a_{\text{Cr}^{2+}}$) is assumed to be $1 \mu\text{mol L}^{-1}$ to obtain the equilibrium potential and compare the influence of the metal complex. The redox potential of $\text{Cr}^{2+}/\text{Cr}(\text{OH})_3$ in the absence of ligand ($E_{\text{Cr}^{2+}/\text{Cr}(\text{OH})_3}$) is described by **Equation 11**:^[53]

$$E_{\text{Cr}^{2+}/\text{Cr}(\text{OH})_3} = E_{\text{Cr}^{2+}/\text{Cr}(\text{OH})_3}^0 - 0.0591 \times 3 \times \text{pH} - 0.0591 \times \log a_{\text{Cr}^{2+}} \quad (11)$$

where $E_{\text{Cr}^{2+}/\text{Cr}(\text{OH})_3}^0$ is the standard potential of $\text{Cr}^{2+}/\text{Cr}(\text{OH})_3$, which is -0.136 V vs. SHE. The redox potential is -0.7 V vs. SHE (-0.4 V vs. RHE) at pH 5, which is sufficiently negative to avoid the reduction of $\text{Cr}(\text{OH})_3$ compared with the potential applied in Figure 6a. Therefore, it is difficult to further reduce $\text{Cr}(\text{OH})_3$ to soluble Cr^{2+} in the absence of ligand.

The standard redox potential is expected to shift due to the formation of a metal complex between Cr^{2+} and ligand following the thermochemical cycle shown in **Figure 7a**. L and β represent the ligand and the formation constant of the metal complex, respectively. The redox potential in the presence of ligand is described by **Equation 12**.

$$E_{\text{Cr}^{2+}L_m/\text{Cr}(\text{OH})_3} = E_{\text{Cr}^{2+}/\text{Cr}(\text{OH})_3}^0 + 0.0591 \times \log \beta - 0.0591 \times 3 \times \text{pH} - 0.0591 \times \log \left(\frac{a_{\text{Cr}^{2+}L_m}}{a_L^m} \right) \quad (12)$$

The first two terms on the right side of the equation are used to obtain the standard potential of $\text{Cr}^{2+}L_m/\text{Cr}(\text{OH})_3$, and the last two terms are used to compensate for the activities

according to the Nernst equation. The bulk activities at equilibrium were obtained from the corresponding equilibrium constants listed in **Table S1** using the HySS program in the pH range of 4 to 6, where the $\text{Cr}(\text{OH})_3$ does not dissolve and the malonate buffer can be a proton donor for HER. The speciation distribution of Cr_{2+} species is shown in **Figure 7b**.

Since malonate buffer can also form a complex with Cr_{2+} , Cr_{2+} -malonate and Cr_{2+} -(malonate)₂ coexist with Cr_{2+} -HEDTA or $\text{Cr}(\text{CN})_{64-}$. Notably, $\text{Cr}(\text{CN})_{64-}$ is a major species in the presence of cyanide at pH 5, while Cr_{2+} -HEDTA remains as a minority. The difference arises from their formation constants (Table S1), where cyanide can form a metal complex more easily than HEDTA. As the pH shifts to more alkaline conditions, deprotonated malonate anions become favorable, which leads to Cr_{2+} -(malonate)₂ predominating in both solutions.

The redox potential obtained from Equation 12 is shown in **Figure 7c**. It is clear that the complexation shifts the redox potential to be more positive and closer to the potential of HER, which supports the enhanced degradation in the presence of metal complex shown in Figure 6. Since $\text{Cr}(\text{CN})_{64-}$ is more favorably formed than Cr_{2+} -HEDTA, the redox potential of $\text{Cr}_{2+}/\text{Cr}(\text{OH})_3$ in the presence of $\text{Fe}(\text{CN})_{64-/3-}$ becomes more positive than that in $\text{Fe}_{2+/3+}$ -HEDTA. This results in a larger driving force to reduce the $\text{Cr}(\text{OH})_3$ layer to soluble Cr_{2+} ions during the stability test. The difference of the redox potentials of $\text{Cr}_{2+}/\text{Cr}(\text{OH})_3$ in the presence of $\text{Fe}(\text{CN})_6$ and Fe -HEDTA becomes similar at pH 6 because Cr_{2+} -(malonate)₂ becomes predominant in both solutions.

Because Cr-malonate complex can also be present, the stability test was performed to identify the effect of malonate anions with bubbling O_2 in a solution of phosphate and malonate buffer at pH 5 (**Figure S4**). Indeed, the current measured at 0 V vs. RHE gradually kept decreasing after 200 min in the presence of malonate buffer, which indicates that ORR started to take place due to the degradation of the CrO_x layer, while the current was maintained close to 0 mA cm^{-2} in the phosphate buffer solution. The formation constant of the soluble Cr_{2+} phosphate complex has not been reported, so the positive potential shift due to complex

formation is not expected in the phosphate solution. The degradation in the malonate buffer solution does not appear to be as severe as in the redox solutions (Figures 6b and c). The difference in reaction kinetics between ORR and redox reduction must be mentioned. The redox reaction is a kinetically facile charge transfer process. Without exposing the Pt surface, a certain amount of leaching Cr may trigger the redox reaction by charge tunneling through the remaining layer. The kinetics of $\text{Fe}(\text{CN})_{64-/3-}$ is approximately two orders of magnitude faster than that of $\text{Fe}_{2+/3+}$ -HEDTA,^[22] which could be another reason why the redox reduction current was severely observed in the presence of $\text{Fe}(\text{CN})_{64-/3-}$. On the other hand, ORR is a kinetically sluggish electrocatalytic reaction that requires adsorbed intermediate to form on the Pt surface. Therefore, a sufficient amount of Cr has to be etched before O_2 molecules are able to reach the Pt surface, which may be one of the reasons why it took more than 200 min before the degradation became obvious in Figure S4. A quantitative description of how much Cr must be leached to observe undesired redox reactions and ORR is beyond the scope of the present work.

The stability of the permselective layer is a remaining problem that is caused by the redox reaction forming a soluble metal complex. To overcome this issue, a redox inactive layer could be a promising candidate, such as SiO_x and TiO_x .^[38–42,54–56] Optimization of the layers' thickness and pore size on a desired substrate is required to prevent the diffusion of redox ions while allowing protons and H_2 to go through.

2.5. Perspective of Ion-Exchange-Membrane-Free Device for Solar-Driven H_2S

Splitting

A stand-alone module was developed for solar-driven H_2 production with the oxidation of redox ion. Since the gaseous product in the electrochemical cells is pure H_2 , CrO_x was employed as a model nano-membrane layer on the selective H_2 evolving cathode while preventing the cross-over of the oxidized redox ion to the cathode. This nano-functionality allows to operate electrochemical reaction without introducing ion exchange membrane, such

as Nafion, whose resistance is expected to be higher in the targeted near-neutral pH range than the acidic condition. This device is an excellent example of the membrane-less electrochemical cell, which has potential to further reduce the cost of the electrochemical device.

The solar-to-hydrogen conversion energy efficiency with sulfide remediation was 1.4%. Majority of efficiency was lost because of the required overpotentials from the original solar-to-electricity conversion efficiency of PV (12%). The overpotentials on both the anodes and cathodes were mainly originated from mass-transport of the reactants. Therefore, reaction conditions, like convection and elevating the temperature, will help to improve the overall efficiency. Although the energy efficiency was still low, the production rate of H₂ was 222 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$, surpassing the H₂ production rate at benchmarking 10% energy efficiency value for solar-driven water splitting (153 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$). Because the required voltage in the present H₂ evolution coupled with redox oxidation is smaller than that for water splitting, higher current density and the resultant production rate of H₂ based on an unit area of the light irradiation can be achieved compared to those for the water splitting.

The stability of CrO_x layer during HER was the major problem in the presence of Fe complex due to the reduction of the layer to soluble Cr²⁺ ions. Redox inactive layers, such as SiO_x or TiO_x, are recommended in the future study. Due to the toxicity of Cr, alternative layers are an urgent need for a variety of electrochemical applications, such as corrosion protection, chlorate production and photocatalytic water splitting. The layers under development for the above mentioned applications will certainly help the present application.

In the present study, Na₂S solution was used as a model sulfide source. It is required to optimize both the electrochemical cells and homogeneous reaction using H₂S gas in future study. Cycle stability of redox solution also needs to be investigated. The existing technique for the homogeneous reaction between sulfide and redox ions will help to design overall redox-mediated H₂S splitting including the separation and purification of sulfur.

3. Conclusion

This study demonstrated a stand-alone module where 14 CIGS-PV cells and 6 EC cells are directly connected in series to produce hydrogen and oxidize Fe^{2+} -HEDTA redox under natural light irradiation. The module was successfully operated below the voltage of the maximum power of the PV cells with a PV-to-EC transfer efficiency of 85%. The rate of H_2 production was 15 mL min^{-1} with an irradiation area of 168 cm^2 ($222 \text{ } \mu\text{mol h}^{-1} \text{ cm}^{-2}$), and its STH conversion energy efficiency coupled with sulfide remediation was 1.4%. Due to the unique thermodynamic characteristics of H_2S , the rate of H_2 production in the present module exceeds the benchmark value ($153 \text{ } \mu\text{mol h}^{-1} \text{ cm}^{-2}$) for 10% of STH conversion energy efficiency for water splitting.

Solid sulfur was obtained by subsequent homogenous reaction between Fe^{3+} -HEDTA and S^{2-} in Na_2S solution instead of H_2S gas for safety reason, which produced a transparent Fe^{2+} -HEDTA solution. This confirmed that the $\text{Fe}^{2+/3+}$ -HEDTA redox ions serve as a reversible charge carriers. The stability of the permselective CrO_x layer remains as a challenge. A series of experiments and thermodynamic studies revealed that the degradation of the CrO_x layer most likely resulted from the reduction of the Cr^{3+} -containing layer into a soluble Cr^{2+} -complex in the presence of ligands. A redox-inactive semipermeable layer is necessary for future work to establish a membrane-less stand-alone system for H_2 evolution.

4. Experimental Section

Materials: All chemicals were purchased with the following purities: KOH (99.99%, Sigma-Aldrich, St. Louis, USA), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (99.0%, Sigma-Aldrich), HEDTA- Na_3 ($\geq 99\%$, Fisher Scientific, Pittsburgh, USA), HEDTA-Fe (99%, Phygenera, Langenberg, Germany), $\text{K}_3[\text{Fe}(\text{CN})_6]$ ($> 99.9\%$, Sigma-Aldrich), $\text{K}_4[\text{Fe}(\text{CN})_6]$ (99.5%, Sigma-Aldrich), KH_2PO_4 (99.995%, Sigma-Aldrich), K_2HPO_4 (99.99%, Sigma-Aldrich), K_2CrO_4 ($\geq 99\%$, Sigma-

Aldrich), $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ (99.995%, Sigma-Aldrich), $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ (99.999%, Sigma-Aldrich), $\text{C}_3\text{H}_4\text{O}_4$ (99%, Alfa Aesar, Ward Hill, USA), and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (98+%, Strem Chemicals, Newburyport, USA). The water used in all experiments was obtained from a Milli-Q Integral system (Millipore, Burlington, USA) with a resistivity of 18.2 $\text{M}\Omega \text{ cm}$. The pH of the electrolyte solutions was adjusted using KOH.

The solution containing Fe^{2+} is sensitive to O_2 , so Ar (99.999%) was bubbled through the solutions before adding salts containing Fe^{2+} , and an Ar atmosphere was maintained. Carbon felt (AvCarb G100 Soft Graphite Battery Felt, thickness 3.2 mm, Fuel Cell Store, College Station, USA) was pretreated in air at 773 K for 5 h to make it hydrophilic.^[57] A Pt black mesh was prepared by chronopotentiometry at 30 mA cm^{-2} for 10 min in a solution containing 72 mmol L^{-1} H_2PtCl_6 and 0.13 mmol L^{-1} $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ after cleaning a pristine Pt mesh (99.99%, wire diameter 0.5 mm, Sigma-Aldrich) in aqua regia for 1 min.^[58] CIGS-PV module (14 cells in series, irradiation area 168 cm^2) was provided from Solar Frontier K.K. Pt was deposited on the SUS mesh (SST 316, 90 mesh, wire diameter 0.0035 inch, FuelCellStore) by sputtering 20 nm of Ti, followed by 50 nm of Pt (Pt/SUS mesh). The custom-made electrochemical module used for the demonstration was made of acrylic sheet (Sumipex®). The redox solution was circulated between the storage bottle and EC module by a peristaltic liquid pump (323, Watson-Marlow) equipped with a pump head (313, Watson-Marlow) at 3 mL min^{-1} .

Electrochemical Measurements: Electrochemical measurements were performed using a BioLogic VMP3 potentiostat (Seyssinet-Pariset, France). Ag/AgCl (saturated KCl) (ALS CO., Ltd Tokyo, Japan) was used as a reference electrode. The potentials were reported with iR_u -correction using an reversible hydrogen electrode (RHE) scale. The uncompensated resistance R_u was measured by impedance spectroscopy (100 mHz – 10 kHz , 10 mV amplitude). CrO_x was deposited on Pt in 0.5 mol L^{-1} K_2CrO_4 solution by chronopotentiometry

at $-10 \text{ mA cm}_{\text{geo}}^{-2}$ for the Pt/SUS or $-100 \text{ mA cm}_{\text{geo}}^{-2}$ for the Pt black mesh for 10 min under Ar atmosphere (99.9999%).

A rotating disk electrode (RDE, 3 mm diameter, ALS CO., Ltd, Tokyo, Japan) of polycrystalline Pt was first polished with 1- μm diamond and then with 0.05- μm of alumina, followed by electrochemical cleaning in a 1 M HClO_4 solution between -0.02 and 1.8 V vs. SHE (standard hydrogen electrode) with bubbling Ar (99.999%). Pt wire was used as a counter electrode. CrO_x was deposited on the Pt RDE in $0.5 \text{ mol L}^{-1} \text{ K}_2\text{CrO}_4$ solution by applying a constant current density of $-280 \mu\text{A cm}^{-2}$ for 10 min with bubbling H_2 (99.9999%).

Homogeneous reaction with sulfide ion: Homogeneous reaction was performed with $0.1 \text{ mol kg}^{-1} \text{ Fe}_{3+}$ -HEDTA in 1 mol kg^{-1} malonate buffer solution ($\text{pH} = 5$) by adding a stoichiometric volume of $0.02 \text{ mol L}^{-1} \text{ Na}_2\text{S}$ solution with mild stirring in Ar atmosphere at room temperature.

Characterization: The kinematic viscosity and density of the electrolyte solutions were obtained using viscometer tubes (cell constants: 0.003259 and $0.009167 \text{ mm}^2 \text{ s}^{-2}$, Fisher Scientific) and a density meter (DM40, METTLER TOLEDO, Columbus, OH, USA), respectively. The conductance was measured using a conductivity meter (S230 and InLab 731-ISM, METTLER TOLEDO). UV-vis spectroscopy was performed using a JASCO model V-670 spectrophotometer with a quartz cuvette and an optical path length of 1 cm . The concentration of Fe redox was diluted to 0.2 mmol L^{-1} before UV-vis measurement. Correspondingly, malonate buffer and Na_2S reference solutions were diluted to 0.2 and 0.1 mmol L^{-1} , respectively. Raman spectra were obtained using an Olympus BXFMILHS microscope with a 785-nm laser.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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References

- [1] B. Zhang, X. Zheng, O. Voznyy, R. Comin, M. Bajdich, F. P. G. De Arquer, C. T. Dinh, F. Fan, M. Yuan, A. Janmohamed, H. L. Xin, H. Yang, *Science* **2016**, *352*, 333–338.
- [2] P. Zhang, L. Li, D. Nordlund, H. Chen, L. Fan, B. Zhang, X. Sheng, Q. Daniel, L. Sun, *Nat. Commun.* **2018**, *9*, 1–10.
- [3] E. Nurlaela, T. Shinagawa, M. Qureshi, D. S. Dhawale, K. Takanabe, *ACS Catal.* **2016**, *6*, 1713–1722.
- [4] J. Crook, A. Mousavi, *Environ. Forensics* **2016**, *17*, 211–217.
- [5] B. You, X. Liu, N. Jiang, Y. Sun, *J. Am. Chem. Soc.* **2016**, *138*, 13639–13646.
- [6] T. Nakajima, A. Hagino, T. Nakamura, T. Tsuchiya, K. Sayama, *J. Mater. Chem. A* **2016**, *4*, 17809–17818.
- [7] K. Fuku, Y. Miyase, Y. Miseki, T. Gunji, K. Sayama, *RSC Adv.* **2017**, *7*, 47619–47623.
- [8] W.-J. Liu, L. Dang, Z. Xu, H.-Q. Yu, S. Jin, G. W. Huber, *ACS Catal.* **2018**, 5533–5541.
- [9] W. Li, N. Jiang, B. Hu, X. Liu, F. Song, G. Han, T. J. Jordan, T. B. Hanson, T. L. Liu, Y. Sun, *Chem* **2018**, *4*, 637–649.
- [10] K. Fuku, Y. Miyase, Y. Miseki, T. Funaki, T. Gunji, K. Sayama, *Chem. - An Asian J.* **2017**, *12*, 1111–1119.
- [11] H. J. Wubs, A. A. C. M. Beenackers, *AIChE J.* **1994**, *40*, 433–444.

- [12] A. L. Kohl, R. B. Nielsen, *Gas Purif.* **1997**, 731–865.
- [13] Y. Kageshima, T. Shinagawa, T. Kuwata, J. Nakata, T. Minegishi, K. Takanabe, K. Domen, *Sci. Rep.* **2016**, 6, 1–12.
- [14] B. G. Ateya, F. M. Alkharafi, A. S. Alazab, A. M. Abdullah, *J. Appl. Electrochem.* **2007**, 37, 395–404.
- [15] a. a. Anani, Z. Mao, R. E. White, S. Srinivasan, A. J. Appleby, *J. Electrochem. Soc.* **1990**, 137, 2703.
- [16] S. Mizuta, W. Kondo, K. Fujii, H. Iida, S. Isshiki, H. Noguchi, T. Kikuchi, H. Sue, K. Sakai, *Ind. Eng. Chem. Res.* **1991**, 30, 1601–1608.
- [17] H. Huang, Y. Yu, K. H. Chung, *Energy and Fuels* **2009**, 23, 4420–4425.
- [18] W. Ma, J. Han, W. Yu, D. Yang, H. Wang, X. Zong, C. Li, *ACS Catal.* **2016**, 6, 6198–6206.
- [19] K. Kim, D. Song, J. I. Han, *Chem. Eng. J.* **2014**, 241, 60–65.
- [20] X. Zong, J. Han, B. Seger, H. Chen, G. Lu, C. Li, L. Wang, *Angew. Chemie - Int. Ed.* **2014**, 53, 4399–4403.
- [21] W. Ma, H. Wang, W. Yu, X. Wang, Z. Xu, X. Zong, C. Li, *Angew. Chemie Int. Ed.* **2018**, 57, 3473–3477.
- [22] K. Obata, L. Stegenburga, Y. Zhou, K. Takanabe, *ACS Sustain. Chem. Eng.* **2019**, 7, 7241–7251.
- [23] J. L. Young, M. A. Steiner, H. Döscher, R. M. France, J. A. Turner, T. G. Deutsch, *Nat. Energy* **2017**, 2, 17028.
- [24] J. Jia, L. C. Seitz, J. D. Benck, Y. Huo, Y. Chen, J. W. D. Ng, T. Bilir, J. S. Harris, T. F. Jaramillo, *Nat. Commun.* **2016**, 7, 13237.
- [25] J. T. Davis, J. Qi, X. Fan, J. C. Bui, D. V Esposito, *Int. J. Hydrogen Energy* **2018**, 43, 1224–1238.
- [26] A. Nakamura, Y. Ota, K. Koike, Y. Hidaka, K. Nishioka, M. Sugiyama, K. Fujii, *Appl.*

- Phys. Express* **2015**, 8, 107101.
- [27] J. Luo, J. H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N. G. Park, S. D. Tilley, H. J. Fan, M. Grätzel, *Science* (80-.). **2014**, 345, 1593–1596.
- [28] Y. Ota, D. Yamashita, H. Nakao, Y. Yonezawa, Y. Nakashima, H. Ebe, M. Inagaki, R. Mikami, Y. Abiko, T. Iwasaki, M. Sugiyama, K. Nishioka, *Appl. Phys. Express* **2018**, 11, 077101.
- [29] T. L. Gibson, N. A. Kelly, *Int. J. Hydrogen Energy* **2008**, 33, 5931–5940.
- [30] W. J. Chang, K.-H. Lee, H. Ha, K. Jin, G. Kim, S.-T. Hwang, H. Lee, S. Ahn, W. Yoon, H. Seo, J. S. Hong, Y. K. Go, J.-I. Ha, K. T. Nam, *ACS Omega* **2017**, 2, 1009–1018.
- [31] A. Fallisch, L. Schellhase, J. Fresko, M. Zedda, J. Ohlmann, M. Steiner, A. Bösch, L. Zielke, S. Thiele, F. Dimroth, T. Smolinka, *Int. J. Hydrogen Energy* **2017**, 42, 26804–26815.
- [32] H. Wang, W. Li, T. Liu, X. Liu, X. Hu, *Energy Convers. Manag.* **2019**, 183, 97–108.
- [33] O. Atlam, F. Barbir, D. Bezmalinovic, *Int. J. Hydrogen Energy* **2011**, 36, 7012–7018.
- [34] M. E. Oruc, A. V Desai, P. J. A. Kenis, R. G. Nuzzo, *Appl. Energy* **2016**, 164, 294–302.
- [35] K. Maeda, K. Teramura, D. Lu, N. Saito, Y. Inoue, K. Domen, *Angew. Chemie Int. Ed.* **2006**, 45, 7806–7809.
- [36] M. Yoshida, K. Takanabe, K. Maeda, A. Ishikawa, J. Kubota, Y. Sakata, Y. Ikezawa, K. Domen, *J. Phys. Chem. C* **2009**, 113, 10151–10157.
- [37] M. Qureshi, T. Shinagawa, N. Tsiapis, K. Takanabe, *ACS Sustain. Chem. Eng.* **2017**, 5, 8079–8088.
- [38] N. Y. Labrador, X. Li, Y. Liu, H. Tan, R. Wang, J. T. Koberstein, T. P. Moffat, D. V Esposito, *Nano Lett.* **2016**, 16, 6452–6459.
- [39] N. Y. Labrador, E. L. Songcuan, C. De Silva, H. Chen, S. J. Kurdziel, R. K.

- Ramachandran, C. Detavernier, D. V Esposito, *ACS Catal.* **2018**, 8, 1767–1778.
- [40] T. Takata, C. Pan, M. Nakabayashi, N. Shibata, K. Domen, *J. Am. Chem. Soc.* **2015**, 137, 9627–9634.
- [41] S. Takenaka, H. Matsumori, H. Matsune, E. Tanabe, M. Kishida, *J. Electrochem. Soc.* **2008**, 155, B929.
- [42] J. A. Bau, K. Takanabe, *ACS Catal.* **2017**, 7, 7931–7940.
- [43] B. Beverskog, I. Puigdomenech, *Corros. Sci.* **1997**, 39, 43–57.
- [44] B. Endrődi, N. Simic, M. Wildlock, A. Cornell, *Electrochim. Acta* **2017**, 234, 108–122.
- [45] T. Shinagawa, K. Takanabe, *J. Phys. Chem. C* **2016**, 120, 1785–1794.
- [46] J. Zheng, Y. Yan, B. Xu, *J. Electrochem. Soc.* **2015**, 162, F1470–F1481.
- [47] T. Shinagawa, K. Takanabe, *J. Phys. Chem. C* **2015**, 119, 20453–20458.
- [48] K. E. Ayers, E. B. Anderson, C. Capuano, B. Carter, L. Dalton, G. Hanlon, J. Manco, M. Niedzwiecki, in *ESC Trans.*, **2010**, pp. 3–15.
- [49] C. V. Philip, D. W. Brooks, *Inorg. Chem.* **1974**, 13, 384–386.
- [50] J. F. Demmink, A. A. C. M. Beenackers, *Ind. Eng. Chem. Res.* **1998**, 37, 1444–1453.
- [51] L. J. Oblonsky, M. P. Ryan, H. S. Isaacs, *J. Electrochem. Soc.* **1998**, 145, 1922.
- [52] T. P. Moffat, R. M. Latanision, *J. Electrochem. Soc.* **1992**, 139, 1869.
- [53] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solution*, National Association Of Corrosion, **1974**.
- [54] C. Pan, T. Takata, M. Nakabayashi, T. Matsumoto, N. Shibata, Y. Ikuhara, K. Domen, *Angew. Chemie Int. Ed.* **2015**, 54, 2955–2959.
- [55] C. Pan, T. Takata, K. Domen, *Chem. - A Eur. J.* **2016**, 22, 1854–1862.
- [56] S. Takenaka, H. Miyamoto, Y. Utsunomiya, H. Matsune, M. Kishida, *J. Phys. Chem. C* **2014**, 118, 774–783.
- [57] K. J. Kim, Y. J. Kim, J. H. Kim, M. S. Park, *Mater. Chem. Phys.* **2011**, 131, 547–553.
- [58] A. M. Feltham, M. Spiro, *Chem. Rev.* **1971**, 71, 177–193.

Figure 1. Schematic image of the solar-driven redox mediated H_2S splitting.

Figure 2. (a) j - V curves measured by chronopotentiometry. (Anode; carbon felt, cathode; CrO_x/Pt -black mesh, static condition, distance between anode and cathode: ~ 5 mm). j - V curve measured by a glassy carbon rotating disk anode is also shown as a reference ($1.0 \text{ mol kg}^{-1} \text{ Fe}^{2+/3+}$ in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, 900 rpm). All the measurements are performed in Ar and 298 K. (b) i - V curve for the CIGS-PV under light irradiation with 1 sun (PV area: 168 cm^2 , 14 PV cells in series).

Figure 3. Pictures of (a) the electrochemical module with 6 EC cells, (b) with anodes, (c) with cathodes, (d) cross-sectional view of anode and cathode, (e) overall picture of the redox-mediated H_2 production under natural light irradiation, (f) schematic image of Figure 3e and (g) the stand alone module.

Figure 4. (a) Current density based on the geometric area of the electrode in the individual cell ($1.8 \times 22.5 \text{ cm}^2$) and Faradaic efficiency of H_2 during the demonstration. (b) i - V curve from CIGS-PV and the voltage measured from the individual EC cells. (Anodes; carbon felts, cathodes; $\text{CrO}_x/\text{Pt}/\text{SUS}$ meshes, 6th Dec 2018, Thuwal, Saudi Arabia).

Figure 5. (a) Raman spectra of precipitate, reference commercial sulfur and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ measured with 785 nm laser. (b) UV-vis spectra of before and after the homogeneous reaction between Na_2S and Fe^{3+} -HEDTA buffered solution. Spectra after oxidizing the supernatant in air are also shown. The inset photographs were taken before the dilution for UV-vis measurements.

Figure 6. (a)-(c) Chronoamperometry using a CrO_x/Pt rotating disk electrode. (d)-(f) Cyclic voltammograms for the CrO_x/Pt electrode before and after the chronoamperometry. Voltammogram measured with a bare Pt electrode is also shown (1600 rpm, pH = 5, 298 K).

Figure 7. (a) Thermochemical cycle between $\text{Cr}(\text{OH})_3$ and Cr^{2+} . (b) Speciation distribution of Cr^{2+} in 1 mol L^{-1} of malonate buffer in the presence of 0.5 mol L^{-1} of $\text{Fe}(\text{CN})_6^{4-/3-}$ or 1.0 mol L^{-1} of $\text{Fe}^{2+/3+}$ -HEDTA obtained by HySS program. The corresponding equilibrium constants are shown in Table S1. (b) Estimated potential-pH diagram for $\text{Cr}^{2+}/\text{Cr}(\text{OH})_3$ in the presence of metal complexes.

ToC

Solar-driven H_2 production coupled with sulfide remediation: A stand-alone module is designed to demonstrate redox-mediated H_2S splitting using an ideal redox charge carrier, Fe-HEDTA, and a nano-membrane coated electrode. $222 \mu\text{mol h}^{-1} \text{cm}^{-2}$ of H_2 production rate is recorded under natural light irradiation, which exceeds the value for benchmark water splitting ($153 \mu\text{mol h}^{-1} \text{cm}^{-2}$ at 10%).

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A Stand-Alone Module for Solar-Driven Redox Mediated H_2S Splitting