Energy-Saving Hydrogen Harvesting from Ethylene oxide /Ethylene glycol (EO/EG) Process Waste Effluent by Electrochemical Reforming

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ABSTRACT

Water electrolysis supported by sustainable electricity has been regarded as the promising method for large-scale hydrogen (H_2) production, but the sluggish anodic oxygen evolution reaction with high-energy barriers to overcome much limited its broad development. Herein, by taking use of the EO/EG process waste effluent, we comprehensively demonstrated the feasibility of developing electrochemical reforming of glycols to simultaneously construct an energy-saving electrolysis H_2 production system and degrade pollutants to purify the effluents. The cathodic H_2 harvesting could retain nearly 100% Faradic efficiency, along with ~ 17.7% gain in electricity and its correlation with the COD removal in the effluent. Furthermore, the electrochemical oxidation of EG was studied in detail under real circumstances and compared with other EG-derived organic substances possibly present in the waste effluent to glean the possible oxidation mechanism. This work provides some new insights for designing both energy-effective electrochemical systems and sustainable water-energy nexus.

Keywords: Hydrogen energy, ethylene glycol, waste effluent, electrochemical reforming, energy-saving

NONMENCLATURE

Abbreviations	
EO	Ethylene Oxide
EG	Ethylene Glycol
COD	Chemical Oxygen Demand
OER	Oxygen Evolution Reaction
DEG	Diethylene Glycol
TEG	Triethylene Glycol

1. INTRODUCTION

Hydrogen (H_2) has attracted increasing attention around the world as one of the most promising substitutes for fossil fuels, encouraging environmental sustainability in the future[1]. Currently, H_2 production via water electrolysis can be a feasible technique, only involving water as the hydrogen source and electricity as the driving power. However, the precious clean water resources (~22 kg H_2O/kg H_2) during water electrolysis can obviously compete with our daily use, whose quality requirement is even higher than that for drinking water[2], and the current cost of water purification is expensive. Additionally, the sluggish kinetics and high thermodynamic barriers in electrochemical water splitting, especially the anodic OER, result in large overpotentials leading to low energy efficiency[3].

EG, one of the central petrochemical chemicals, plays a crucial role in downstream chemical production and economic development[4]. The EG production process uses the conventional EO hydration reaction. Water is usually over-supplied to improve the EG production selectivity (molar ratio H_2O: EO = 20-25: 1).

The EO/EG process unit inevitably generates a large amount of waste effluent containing high COD(2-20 g/L) due to the presence of mono ethylene glycol and its condensation derivatives as well as aldehydes[5]. Thus, the bottom waste effluent of the reactor is usually included in the list of hazardous waste and needs special treatment[6]. At present, the treatment of EO/EG waste effluent has many problems, for example, using PVA granular sludge expansive bed reactor can produce CO_2 and consume a large amount of recycled water (up to 10 million tons per year) to dilute the waste effluent. In fact, this waste effluent features abundant glycol substrates and favorable thermodynamic potentials[7-9]. It has a theoretical potential of -0.81 V (vs. RHE), and thus could replace sluggish anodic OER to pair with the cathodic H_2

production half-reaction, constructing an energy-saving electrolysis system. Moreover, the use of glycol substrates can be oxidized in versatile Ni-based electrocatalytic system into value-added carboxylate products and eliminate the explosive H_2/O_2 mixture product to substantially increase the safety[10-12].

Herein, electrochemical reforming of glycols was developed to withdraw H_2 from the actual waste effluent during EO/EG producing process to control pollution. To better understand the reforming system, the hierarchical anodes $(Ni(OH)_2/NF)$ were delicately fabricated to investigate the electrochemical oxidation towards different concentrations and simulated waste effluent, deciphering C-C bond cleavages, effect of different ions and elements, electricity efficiency, H_2 production and COD removal during the long-time electrolysis. This work effectively opens up a brand-new perspective and shows strong competitiveness in future sustainable water-energy-ecosystem nexus[13-15].

2.   RESULTS AND DISCUSSION

The industrial production of EG is classified into several strategies according to the raw materials from coal, natural gas, and petroleum. Among these production methods, the petroleum pathway occupies almost 80%-90% of the worldwide EG production and has been adopted in many countries. In this pathway, the obtained ethylene from petroleum refining is injected with oxygen under Ag-based catalysis to generate the EO product. Ethylene epoxidation and EO hydration combined process is the most important and mature process route for petroleum-based EG production (Fig. 1)[16].

1-EO synthesis 2-CO$_2$ absorber column 3-CO$_2$/EO separator column 4-EO refining column 5-EG feed tank 6-Hydration recctor 7-Multiple stage evaporator 8-Washing tower 9-EG refining column 10-DEG refining column 11-TEG refining column
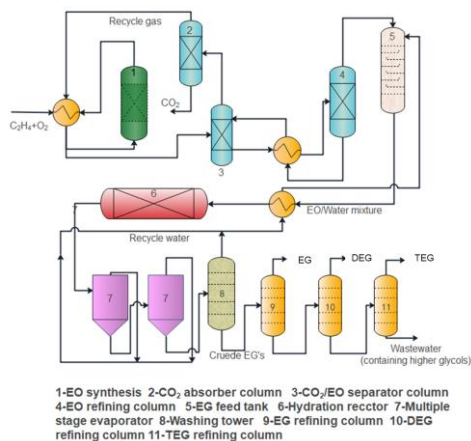
Fig. 1. Illustration diagrams of EO/EG process unit in the direct catalyzed hydration

The global production capacity is about 24 million tons per year, accounting for 50-60% of the total EG production capacity. EG product through EO hydration is at the level of 10-15 wt%, and multiple evaporations are consequently carried out to get highly purified EG products (>98%). Therefore, the generation of EG is always accompanied with a certain amount of organic containing waste effluent discarded during the production process. Generally, it is sent to special treatment departments with charge, resulting in much burden on the environment and expense.

According to the component analysis of an EO/EG waste effluent sample, EG and DEG were the major organic component present in the waste effluent with small amounts of TEG and alkyl species, which may be derived from the residual organics during the hydration process without evaporation(Table S1).

The element analysis results revealed that large amounts of Na, K, and Fe were present and Cl^-, NO_3^- and SO_4^{2-} ions were also accompanied in the waste effluent (Table S2), which possibly originated from the corrosion of pipes and impurities of raw materials.

Considering the abundant organic glycol species in the EO/EG waste effluent, its oxidation could be an alternative anodic reaction to the sluggish OER in water electrolysis(Fig. S1). An electrochemical deposition method was adopted to obtain $Ni(OH)_2$ onto the porous nickel foam $(Ni(OH)_2/NF)$ as the active electrodes. During this process, the porous nickel foam substrate was placed in a nickel(II) salt solution and was held at a negative potential to elicit a cathodic current from the reduction of water, while nickelous ions could simultaneously react with the generated OH^- to form $Ni(OH)_2$ onto the substrate[17].

The surface morphology was first characterized by SEM and TEM(Fig. S2). The deposited materials exhibited an aggregated status with abundant pore across the particles, with some branches interlocked on the surface High-resolution TEM images revealed a lower crystallinity with a lattice fringe of 0.220 nm ascribed to the (200) facet. This phenomenon was also revealed by the XRD characterization (Fig. S3(a)), as indicated by the absence of new peaks after electro-deposition. It could demonstrate that the surface-active layers mostly presented as amorphous structures, which have often been considered to be active for electrocatalysis[18]. By comparing the Raman signals before and after electro-deposition (Fig. S3(b)), some characteristic peaks assigned to the $Ni(OH)_2$ species emerged, where the signals at 3582 cm^{-1}, 1553 cm^{-1}, 840 cm^{-1}, and 452 cm^{-1} were separately assigned to symmetric stretching mode of the hydroxyl groups (vO-H), the deformation vibrations of the water molecule hydroxyl groups (δ-OH),

the rotational Eg(1) mode and translational A1g(1) stretching mode of the Ni(OH)$_2$ phases[19]. XPS characterizations were also conducted to study the surface chemical status before and after electro-deposition. From the high-resolution Ni 2p$_{3/2}$ spectra, there were three peaks present at the binding energy of 852.0 eV, 853.5 eV and 856.2 eV, ascribed to metallic Ni^0, surface NiO, and Ni(OH)$_2$ species respectively[20]. It reflected an increased content of Ni(OH)$_2$ species from 58.6% to 72.5% after electro-deposition (Fig. S3(c) and Table S3). The high-resolution O1s spectra were deconvoluted into lattice oxygen (529.1 eV), surface hydroxy-oxygen (531.6 eV), and loosely bound adsorbed oxygen (533.2 eV), such as adsorbed O$_2$ and/or H$_2$O[21]. After electro-deposition, the percentages assigned to surface hydroxy-oxygen and adsorbed oxygen species were elevated (Fig. S3(d) and Table S4). The increased surface hydroxy-oxygen species was derived from the formed Ni(OH)$_2$, while the promoted adsorbed oxygen could be indicative of improved hydrophilicity[22] or the defective nature of deposited materials. These evidences could simultaneously demonstrate the successful Ni(OH)$_2$ decoration on the porous NF framework by the electro-deposition strategy.

By using the obtained Ni(OH)$_2$/NF electrode as the anode, we conducted LSV measurement and compared the kinetics in 1 mol/L KOH with/without waste effluent addition (Figure 2(a)). The synthesized Ni(OH)$_2$/NF electrode presented an oxidation peak starting at ~1.36 V ascribed to Ni^{2+}/Ni^{3+} redox, after which the OER current began to rise slowly. In comparison, the original Ni^{2+}/Ni^{3+} redox disappeared in the presence of waste effluent, and meanwhile the current density was drastically elevated at this position. This phenomenon was in accordance to previous literatures that the potential of organic oxidation was coupled with Ni^{2+}/Ni^{3+} conversion to obviously boost the electrochemical activity, 170 mV ahead of the OER half-reaction[23]. Additionally, we also carried out a series of dilution experiments to investigate the optimal concentration of waste effluent. The current density was raised and over-potential was reduced with waste effluent dilution times decreasing from 500 to 100. However, when the waste effluent dilution times were further decreased from 100 to 20, the current density demonstrated a gradual descending tendency and the reversed for the overpotentials (Fig. 2(c-d)). It could be ascribed to the limited reactive sites and excessive organic substances present could induce competitive adsorption to inhibit the effective interface charge transfer. We also considered the COD removal of waste effluent after the 4 hr electrolysis. The removal rate

followed a similar trend as the overpotential or the current density. The optimal dilution range was estimated to be near 50 times dilution. Under this dilution range, organic matter could be properly adsorbed on the electrode surface without causing vicious competition between organic matter molecules.
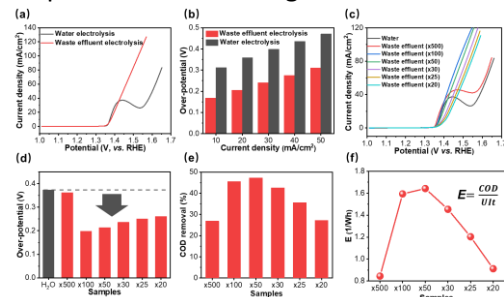

Fig. 2. (a) LSV curves of Ni(OH)$_2$/NF in 1 M KOH electrolyte with/without waste effluent addition, and (b) their corresponding over-potentials under different current density; (c) LSV curves of Ni(OH)$_2$/NF in 1 M KOH electrolyte with different dilutions of waste effluent addition, and (d) their corresponding over-potentials at 50 mA/cm^2;(e) COD removal of the waste effluent after 4 hr electrolysis, and(f) relationship between waste effluent concentration.

During 4 hr electrolysis, the electrochemical current density of Ni(OH)$_2$/NF exhibited ignorant decreases in the alkaline waste effluent electrolyte (Fig. 3(a)).The color of waste effluent electrolyte also changed from dark brown to light yellow. According to the cathodic H$_2$ generation at different durations, the correlations of H$_2$ amount and Faradaic efficiency with total charges were established respectively (Fig. 3(b)). The amount of H$_2$ production collected at the cathode was linearly scaled with the total charges, achieving nearly 100% Faradaic efficiency. This validly proved no interference of impurities present in the waste effluent on the HER half-reaction. During the electrolysis process, the COD removal efficiency kept upgraded to indirectly reflect the partial degradation of organic substance contained. The content of alcoholic organics in the electrolyte decreased significantly with the generation of organic acid salts(Table S5). In addition, there was an energy-saving electricity of 17.7% by replacing water electrolysis with alkaline waste effluent electrolysis. These above results demonstrated the feasibility of EO/EG process waste effluent applied in organic removal to assist energy-efficient electrocatalytic H$_2$ production.
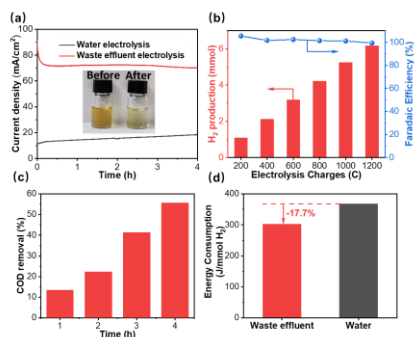
Fig.3. (a) 4 hr electrolysis of Ni(OH)$_2$/NF in 1 M KOH electrolyte with/without waste effluent addition(final discharge of heavy alcohol effluent), and (b) the corresponding amount of H$_2$ production and Faradaic efficiency under different charges; (c) COD removal of the waste effluent electrolyte mixture during the electrolysis process, and (d) the energy consumption comparison per molar H$_2$ product between alkaline waste effluent and water electrolysis.

Referring to the waste effluent component analysis, EG was selected as the model substrate to simplify from the complicated waste effluent. CV curves showed a consistent trend compared to that in the real waste effluent, in which the current density was obviously higher than that without EG by 216 mV ahead at 100 mA/cm^2. The onset potential also overlapped with the Ni^{2+}/Ni^{3+} redox potential. The electrochemical activity could further be improved with the amount of Ni(OH)$_2$ (Fig. 4(b)) materials, proving that Ni(OH)$_2$ species played a critical role. In contrast with commercial dimensional stable anode or precious metal electrodes, the prepared Ni(OH)$_2$/NF electrode performed much superior electrochemical activity (Fig. 4(c)).
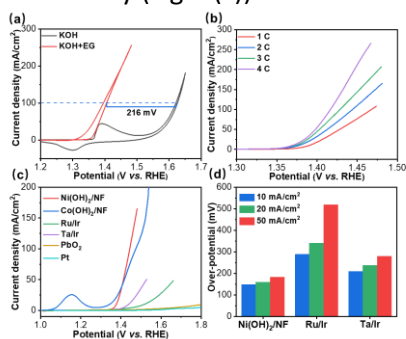

Fig. 4. (a) CV curves of Ni(OH)$_2$/NF in 1 M KOH electrolyte with/without 0.2 M EG addition, and LSV curves in the presence of 1 M KOH and 0.2 M EG :(b)under different charge amount electro-deposited; (c) different electrodes; (d) over-potentials for three typical electrodes under different current densities.

Through product analysis under different electrolysis time, we found that the formate (FA) and oxalate (OA) were generated with depleting EG. The Faradaic efficiencies of FA and OA versus time exhibited an opposite trend (Fig. S4). On the basis of these clues and previous literature and chromatographic analysis[24-26], after studying the Faraday efficiency of oxidation products of several possible products(Fig. S5), we inferred that the electrochemical oxidation of EG on the Ni(OH)$_2$/NF electrode could be classified into several steps as described in Fig. 5. Initially, EG was adsorbed on the Ni(OH)$_2$/NF electrode surface and subsequently electrochemical oxidation could take place to generate corresponding products or intermediates.
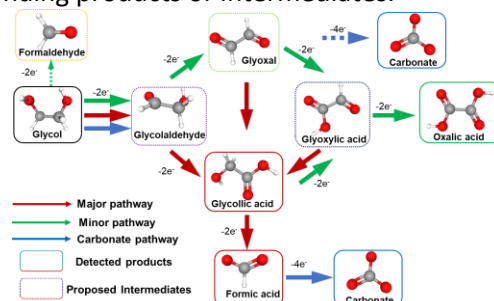

Fig.5. The plausible mechanism towards EG electrooxidation on the Ni(OH)$_2$/NF electrode.

EG could be firstly oxidized to an aldehyde intermediate,glycolaldehyde may be an important branching point of oxidation to downstream products. Otherwise it could be gradually converted through dehydrogenation into glycolic acid and FA intermediates. The formed glycolic acid intermediates are not stable enough on the active Ni(OH)$_2$/NF surface and easily broken up into FA to achieve complete mineralization as carbonate. In another pathway, the formed glycolic acid could be mildly oxidized into glyoxylic acid and OA. The electrochemical oxidation of EG under different pathways could be dependent on a combination of parameters[13, 27].

Considering the impurities in the real waste effluent, the influence of several key impurities on the electrochemical activity of EG oxidation were investigated(Fig. S6). These results conclude that abundant impurity ions could induce severe effects on the electrochemical performance, increase the electricity energy burden and reduce the H$_2$ production efficiency, which means that these interferences should be carefully dealt with and removed for practical applications.

Since different organic substances could exhibit distinctive behaviors of electrochemical oxidation, we compared the LSV curves of three typical glycols in the waste effluent (Fig. 6(a)), and the results indicated that the electrochemical activity was reduced for the more complicated organic component. Through collecting the cathodic H$_2$ production and monitoring COD variation, we observed that the efficiency of COD removal and

amount of H_2 production were positively correlated in three organic substances (Fig 6(d)). Referring to the analysis results in actual EO/EG waste effluent, we attempted to mix the key organic components to simulate the waste effluent into the KOH electrolyte. The LSV curves under different electrolyte in both simulated and actual waste effluent showed the increased current density and the advances in the onset potentials (Fig. 6(e)). H_2 production and COD removal results in both electrolytes revealed superior performance compared to the traditional alkaline water electrolysis, especially several orders of magnitude higher in the H_2 generation efficiency. The overall performances in the actual waste effluent were not as satisfactory as those in the simulated waste effluent, which should be carefully considered in terms of the interfering substances. Since a larger electrode area could contribute more reactive sites, we observed an increased COD removal and H_2 production with the expanded electrode area (Fig. 6(c)), greatly inspiring promising potential in large-scale practical applications. Overall, this strategy of utilizing EO/EG waste effluent to electrochemical reforming for energy-efficient H_2 harvesting has been proven feasible and effective. It would be an alternative layout to the resource economy for carbon neutrality, and more related works on the optimization of the pilot test and field application will appear soon or later.
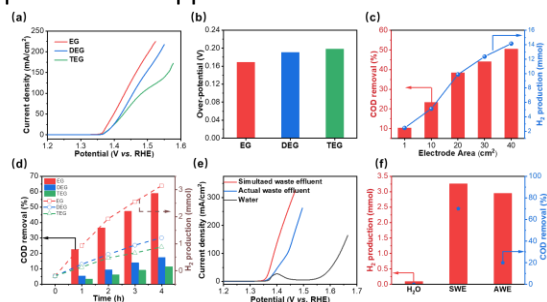

Fig.6. (a)LSV curves and(b)corresponding over-potential (50 mA/cm^2) of 0.2 MEG, DEG or TEG in 1 M KOH;(c) the effect of electrode area on COD removal rate in alkaline simulated waste effluent electrolyte, and (d) the comparison of COD and H_2 production versus electrolysis time in presence of EG, DEG or TEG;(e) LSV curves of different water;(f) comparisons of COD and H_2 production for 4 hr under corresponding conditions.

3. CONCLUSION

In summary, we have comprehensively investigated the main content of EO/EG process waste effluent and attempted to apply into alkaline water electrolysis as the organic substance to replace the sluggish OER half-reaction for energy-efficient H_2 production. The facilely-obtained Ni(OH)$_2$/NF electrode was employed as the active anode, and the alkaline waste effluent oxidation obviously enhanced the electrochemical activity. Moreover, the cathodic H_2 harvesting was not disturbed with nearly 100% Faradic efficiency, along with ~ 17.7% gain in electricity and it correlated with the COD removal in the electrolyte. Through adopting EG as the model substance, we obtained more detailed insight into the electrochemical mechanism and found several key factors influencing the performance. According to the simulated component in waste effluent, the effectiveness of organic substance-assisted water splitting has been decreased with the organic residue changing from EG, DEG to TEG. Furthermore, there are some in situ hydrogen use scenarios for the ethylene glycol industry such as the mono-hydrogenation of ethylene glycol to produce glycolide and polyethylene glycol hydrogenation refining. It should be concerned that under a highly oxygen-rich environment, the introduction of reductive reactions requires safety considerations. This work not only broadens the electrochemical H_2 generation system but also paves a solid way to build a more sustainable development society.

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