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Green Hydrogen Production from Seawater Using Metal Oxide Catalysts

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ABSTRACT

In this work, five electrodes were studied to produce green hydrogen (GH) versus the graphite electrode (as a positive electrode). The electrodes are Fe, Cu, Al, Zn, and Pb. It was found that Zn electrode produces the most hydrogen from seawater, then Pb, the least ones are Fe, Cu, and Al. Oxides (Cu2O, Cr2O3, V2O5, ZnO, SnO2, Pb3O4, NiO, MnO2, Fe3O4, and SiO2) were used and added at a fixed concentration to the five electrodes, and the extent of the effect of these oxides on the production of GH were studied. Some of them were inhibitory, some were a helpful factor and worked to stimulate the production of GH, and some had no effect. However, most oxides inhibit hydrogen production at the Al electrode, most of them did not affect H2 production at the Fe and Cu electrodes, while oxides such as ZnO, SnO2, Pb3O4, NiO, MnO2, and Fe3O4 showed an increase in H2 production at the zinc electrode. On the contrary, V2O5, SnO2, and SiO2, were found to increaseH2 production at the zinc and Pb electrodes.

KEYWORDS: metal oxides - Huffman voltammeter - sea water - catalysts - green hydrogen.

1. INTRODUCTION

Electrolysis is used to produce green hydrogen (GH) and is considered an environmentally friendly solution to reduce carbon emissions and preserve the environment. GH is produced through the electrolysis of freshwater supported by renewable energy systems to reduce the emission of CO2 gases. Therefore, a large amount of freshwater is used to produce H2 at the cathode and O2 at the anode. It is preferable to use seawater because it is the most abundant water source. However, the obstacles are the reaction of unwanted chlorine gas at the anode and the resulting corrosion. The development of effective chemical catalysts of oxides for non-precious metals with industrial current density is important for the production of H2 from acidic or alkaline water/seawater in order to alleviate the energy crisis and environmental pollution. Hydrogen is considered a promising source of renewable and green energy to meet energy needs and achieve the prevention of carbon dioxide emissions. It is, therefore, preferable to use abundant and relatively cheap seawater as opposed to fresh water. However, the production of highly effective and efficient chemical and electrocatalysts with long-term viability under harsh corrosive conditions remains a challenging topic for large-scale seawater electrolysis technology.

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Transition metal electrocatalysts for hydrogen production fall into four different classes, namely alloys, layered double hydroxides (LDHs), transition metal dichalcogenides (TMDs), and single-atom catalysts (SACs) [1]. Pt-MoP-MoO3/C an efficient electro-photo catalyst was constructed to enhance Pt catalytic capacity via the uniform integration of Pt nanoparticles and MoP on carbon black (Vulcan-C), in which Vulcan-C was used as a support material [2]. Ga doped $Co_{0.6}Cu_{0.4}Fe_2O_4$nano catalysts was fabricated via sol-gel auto-combustion (SGA) for the production of GH generation [3]. Ni species were deposited as a single atom onto TiO2/g-C3N4 (TCN) composite photocatalyst with an S-scheme heterojunction to produce H2 [4]. Alloy, noble metals, transition metals, carbides, oxides, nitrides, phosphides, synthesis of novel catalysts, and especially the design for seawater electrolysis are prospected [5]. Rare earth compounds, N-doped carbon and bimetallic carbide were demonstrated to accelerate the H2 evolution process in acid-base electrolytes and seawater [6]. A carbon-based composite photocatalyst (CQM) was fabricated for photocatalytic production of H2O2. The metal ions strongly affect the photocatalytic activity of the CQM catalyst with the order of Mg2+> Al3+> Ca2+> K+ [7]. Cr–Cu2S Nanoflakes supported on Cu-foam (Cr–Cu2S-CF) for alkaline water electrolyze for H2 production at an industrial scale [8]. In addition, Ni-doped WO2 was proposed to realize H2 production from seawater, Ni doping can enhance the H2 evolution reaction activity of WO2 with excellent inhibitor corrosion [9]. A ternary Pt, Ru, and Ti (PRT) catalyst with a minimized Pt level

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(Pt0.06Ru0.24Ti0.7Ox) drives chloride oxidation reaction (ClOR) at a Faradaic efficiency (FE) of ~100% in saline water at current density [10]. Co/W5N4 catalyst with porous structure is innovatively constructed [11]. The self-supporting electrode is prepared by in-situ growth of nickel and boron on porous hydrophilic filter paper (HP) via mild electroless plating at 298 K [12]. Indeed, the existence of various ions in seawater is a barrier to efficient H2 production via photocatalytic splitting [13]. Co/Co9S8 electrocatalyst with hollow spherical structure. As-prepared material exhibited excellent electrocatalytic activity in H2 evolution reaction (HER) in alkaline seawater [14]. A bifunctional Ni foam supported NiFe2O4was as spinel catalyst (i.e., NiFe2O4/NF) that is capable of facilitating the coupling of (HER) with selective methanol oxidation reaction (SMOR) in seawater to produce format via a CO-free pathway [15]. N and P doped carbon nanoparticles decorated with tiny amounts of Pt nanoparticles (~6.0 wt%) were synthesized and investigated for the catalytic performances to H2 and Cl2 generation from fresh and seawater [16]. Moreover, strong metal-support interaction (SMSI) and Pt-p-block alloys (PtM-CNT, M = Ga, In, Pb, and Bi) to construct a stable electronic perturbation and achieve acidic seawater H2 evolution [17]. CoSe2-CoO/CF catalysts are prepared by a simple electrodeposition method [18]. Carbon-encapsulated Pt was fabricated core-shell supported CoMo2S4-NGNF as an efficient electrocatalyst for the H2evolution reaction (HER) [19]. The unique 3D nano-rose structure and the optimized electronic structure of the heterostructure enable Ni2P/Co(PO3)2/NF super-hydrophilic and super-aerophobic characteristics, and highly facilitate (HER) kinetics in alkaline seawater [20]. P-Ni4Mogrow on the surface of the copper foam (CF) substrate to synthesize an efficient seawater electrolysis catalyst (P-Ni4Mo/CF) [21]. Se/NiSe2 was developed to exhibit energy saving for alkaline seawater splitting in urea [22]. A highly conjugative π-acceptor type ligand with metal ions (M = Co2+, Zn2+, Cu2+ and Ni2+) was used as a catalyst for the evolution of H2 as alternate fuel [23]. Ru, P dual-doped NiMoO4 multichannel nanorods in situ grown on nickel foam (Ru/P-NiMoO4-NF), which can achieve chlorine-free H2 production [24]. High-performance catalysts were designed for seawater electrolysis [25]. Wind energy is used for the electrolysis method used in H2 production [26]. An Egyptian Atlas for GH production utilizing water electrolysis powered by the available wind (wind turbines, WTs) and solar (PV panels) energies [27]. Offshore Wind Technology (OWF) was used for H2 production through water electrolysis, as well as the storage and transportation of the produced H2 for use in H2 fuel stations [28]. The reaction between metal scrap and steam is studied for H2 production, the scrap materials are used as nanomaterials in the generation of GH, and the production pathways for nanomaterials have also been addressed [29]. The most significant challenge in the thermally driven reaction is finding a metal oxide that can be reduced at practical temperatures with acceptable reaction kinetics, whereas, the most important challenge for photocatalytic reactions is to find a stable semiconductor-based material capable of splitting water using a large fraction of sunlight [30]. Metal-oxide electrocatalysts, including noble metal oxides, non-noble metal oxides and their compounds, and spinel- and perovskite-type oxides, for seawater splitting. We elucidate their chemical properties, excellent the oxygen evolution reaction OER selectivity, [31] the nonmetallic electrode is made of surface rock portions that have high porosity and pore volume and high permeability and pore connectivity and is saturated with saline water. Surface rocks with the above properties exhibit very low resistivity and hence conduct electricity like metallic electrodes [32], the Novel Solution. A low-cost but powerful solution to the corrosion problem is introduced, tested, and experimentally proved. The novelty of the solution relies on replacing the classic special high-cost metallic positive electrode with a nonmetallic, no-cost, one. The nonmetallic electrode is made of surface rock portions that have high porosity and pore volume and high permeability and pore connectivity and is saturated with saline water. Surface rocks with the above properties exhibit very low resistivity and hence conduct electricity like metallic electrodes. The voltage and the current conducted by such electrodes are controlled by the electrode geometry.

In this work, five electrodes were studied to produce GH versus the graphite electrode (as a positive electrode). The electrodes are Fe, Cu, Al, Zn, and Pb. It was found that the Zn electrode produces the most H2 from seawater.

2. THE EXPERIMENT

2.1. Materials and Chemicals:

Five different electrodes 3cm in length and 2ml diameter (0.1cm2) for product H2 (Fe, Cu, Al, Zn and Pb) against graphite electrode at Hoffman Voltammeter (Picture 1) with modified the cathode electrode to put 1g of 10 metal oxides as the catalyst: Cuprous oxide (Cu2O), Chromium (III) oxide (Cr2O3), Vanadium pentoxide (V2O5), Zinc oxide (ZnO), Stannic oxide (SnO2), Red lead oxide (pb3O4), Nickle oxide (NiO), Manganese dioxide (MnO2) black iron oxide (Fe3O4) , and Silicon Oxide (SiO2) are used, 3.5% NaCl as seawater electrolyte solution, DC electric source.

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Picture 1: Hoffman Voltammeter

2.2. Method

The Huffman voltmeter is connected to a 5–12-Volt direct current source with different electrodes without adding a catalyst and measuring the amount of H2 produced. Then, after an hour, add a specific concentration of the catalyst and measure the percentage of H2 produced at the same time, with the same electrodes, and change the catalysts. The volumes of H2 gas produced were as in the following table:

Table 1. The volume by ml of H2 product /h.cm2 at different electrodes with ten metal oxides.

C/H_2	nil	Cu_2O	Cr_2O_3	V_2O_5	ZnO	SnO_2	Pb_3O_4	NiO	MnO_2	Fe_3O_4	SiO_2
Fe	8 ml	5	6.5	3.1	8	8	3	1	2.5	7	7
Cu	11.2	10	14.5	12	13.7	8	13.2	14	13.4	12.5	13.2
Al	20	11	6	2.5	13	10	7	4.3	8.5	5.5	17.5
Zn	42	7	30	5	60	60	58	57	60	57	28.2
Pb	36	28	31	59	26	56.3	8	40	42.3	14.3	60

3. RESULTS AND DISCUSSION

Fig. 1 depicts the sequence of electrodes that yield the highest hydrogen (H2) production without the utilization of oxides as catalysts or inhibitors. These electrodes are ranked as follows: Zn, Pb, Al, Cu, and Fe. Additionally, it is observed that Cu2O functions as an inhibitor of H2 production at the Zn electrode, with its inhibitory effect diminishing progressively at the Pb and Al electrodes, and being least pronounced at the Cu and Fe electrodes.

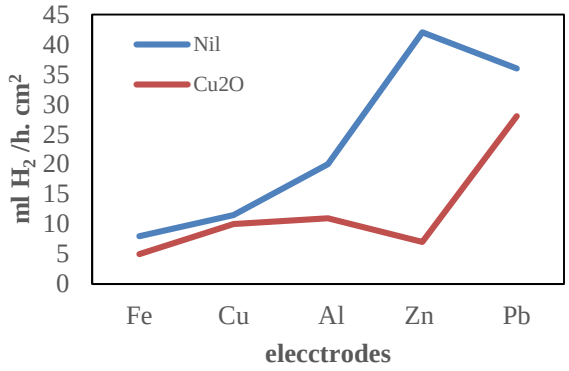


Fig.1. The effect of Cu2O for production of H2 at electrodes.

Figure 2 illustrates that Cr2O3 serves as an inhibitor of hydrogen (H2) production at the aluminum (Al) electrode. Conversely, its impact is less pronounced at zinc (Zn) and lead (Pb) electrodes, and it has no effect on copper (Cu) and iron (Fe) electrodes.

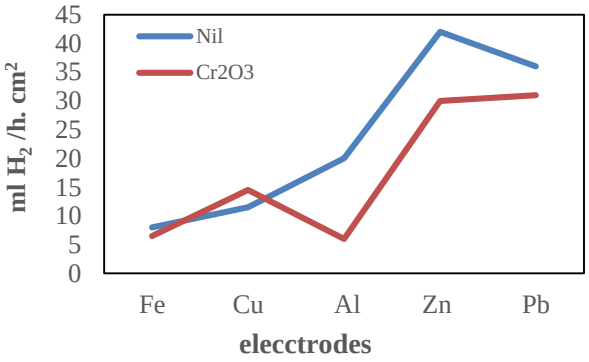
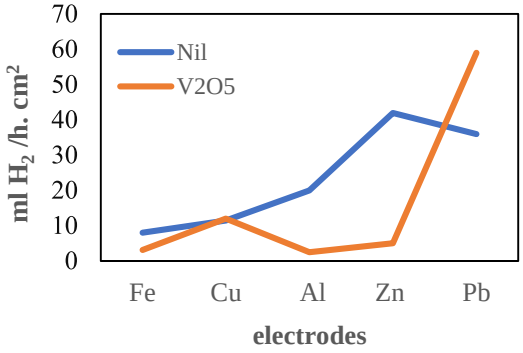


Fig.2. The effect of Cr2O3 on the production of H2 at electrodes.

Fig. 3 demonstrates that V2O5 functions as a catalyst for hydrogen (H2) production at the lead (Pb) electrode. Conversely, it acts as an inhibitor for H2 production at the zinc (Zn) and aluminum (Al) electrodes, while it has no effect on H2 production at the copper (Cu) and iron (Fe) electrodes.



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Fig.3. The effect of V2O5 on the production of H2 at electrodes.

Fig. 4 illustrates that ZnO serves as a catalyst for hydrogen (H2) production specifically at the zinc (Zn) electrode. However, it does not exert any influence on H2 production at the lead (Pb), aluminum (Al), copper (Cu), and iron (Fe) electrodes.

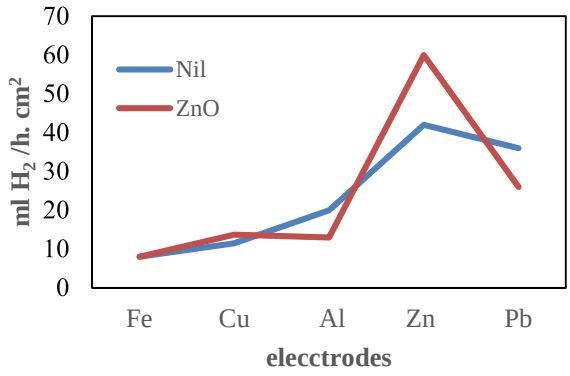


Fig.4. The effect of ZnO on the production of H2 at electrodes.

Fig. 5 displays that SnO2 functions as a catalyst for hydrogen (H2) production at both the lead (Pb) and zinc (Zn) electrodes. Conversely, it acts as an inhibitor at the aluminum (Al) electrode and has no effect on H2 production at the copper (Cu) and iron (Fe) electrodes.

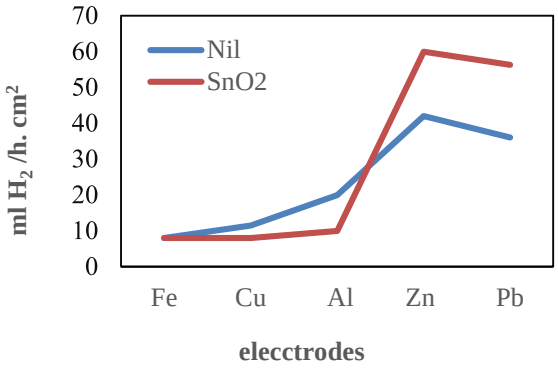


Fig.5. The effect of SnO2 on the production of H2 at electrodes.

Fig. 6 demonstrates that Pb3O4 serves as an inhibitor of hydrogen (H2) production at both the lead (Pb) and aluminum (Al) electrodes. Conversely, it acts as a catalyst at the zinc (Zn) electrode and has no effect on H2 production at the copper (Cu) and iron (Fe) electrodes.

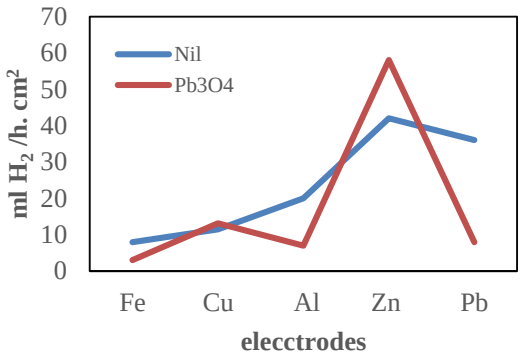


Fig.6. The effect of Pb3O4 on the production of H2 at electrodes.

Fig. 7 illustrates that NiO functions as an inhibitor of hydrogen (H2) production specifically at the aluminum (Al) electrode. Conversely, it acts as a catalyst at the zinc (Zn) electrode and does not affect H2 production at the copper (Cu) and iron (Fe) electrodes.

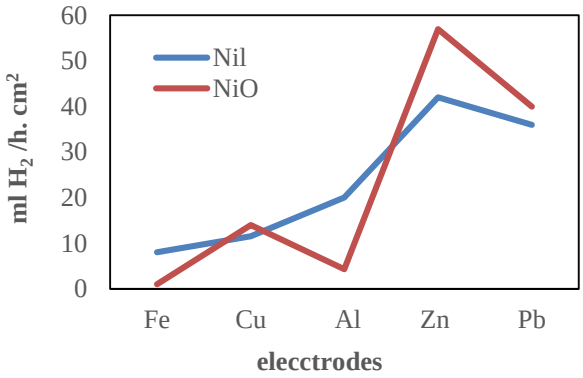


Fig.7. The effect of NiO on the production of H2 at electrodes.

Fig. 8 demonstrates that MnO2 serves as an inhibitor of hydrogen (H2) production specifically at the aluminum (Al) electrode. Conversely, it acts as a catalyst for H2 production at the zinc (Zn) electrode and has no effect on H2 production at the lead (Pb), copper (Cu), and iron (Fe) electrodes.

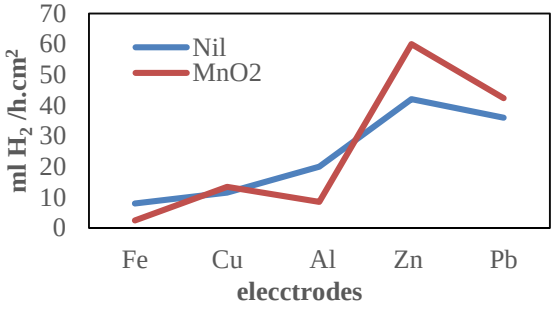


Fig.8. The effect of MnO2 on the production of H2 at electrodes.

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Fig. 9 demonstrates that Fe3O4 serves as an inhibitor of hydrogen (H2) production specifically at the aluminum (Al) electrode. Conversely, it acts as a catalyst for H2 production at the zinc (Zn) electrode and has no effect on H2 production at the lead (Pb), copper (Cu), and iron (Fe) electrodes.

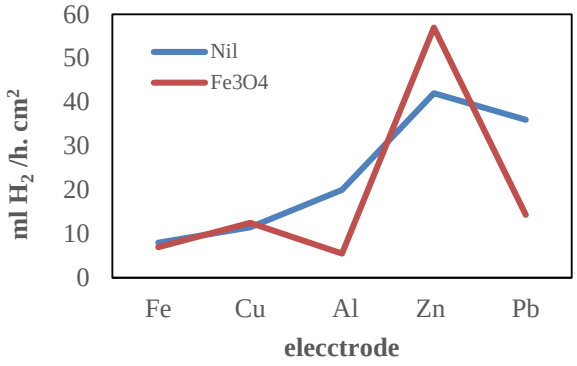


Fig.9. The effect of Fe3O4 on the production of H2 at electrodes.

Fig. 10 illustrates that SiO2 acts as a catalyst for hydrogen (H2) production specifically at the lead (Pb) electrode. Conversely, it functions as an inhibitor at the zinc (Zn) electrode and has no effect on H2 production at the aluminum (Al), copper (Cu), and iron (Fe) electrodes.

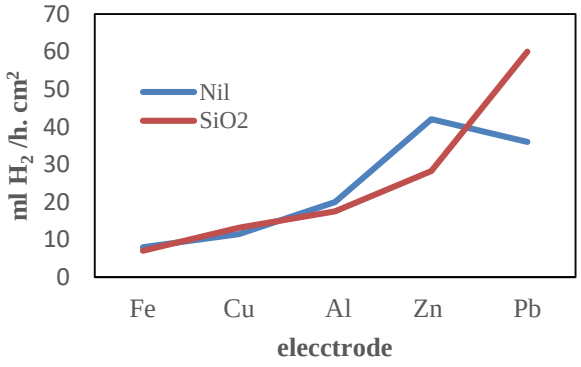


Fig.10. The effect of SiO2 on the production of H2 at electrodes.

Fig. 11 illustrates that the metal oxides NiO, MnO2, Pb3O4, V2O5, Cu2O, and Cr2O3 function as inhibitors at the iron (Fe) electrode. On the other hand, ZnO, SnO2, Fe3O4, and SiO2 have no effect on the Fe electrode.

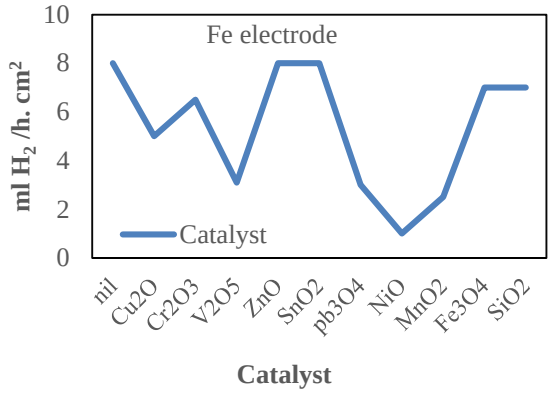


Fig.11. The effect of metal oxides at Fe electrode.

Figure 12 demonstrates that the metal oxides SnO2 and Cu2O act as inhibitors at the copper (Cu) electrode, whereas ZnO, Fe3O4, Cr2O3, NiO, MnO2, Pb3O4, V2O5, and SiO2 exhibit relatively weak effects at the Cu electrode.

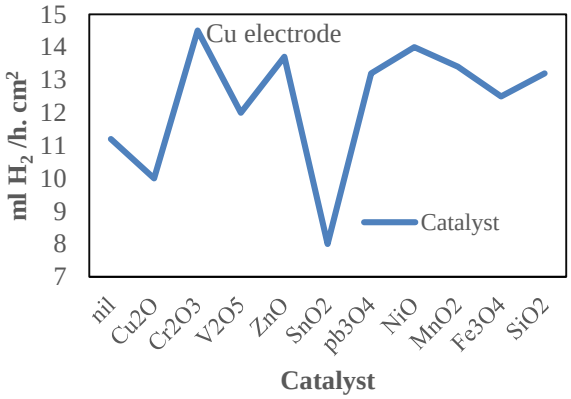


Fig.12. The effect of metal oxides at Cu electrode.

Fig. 13 illustrates that the metal oxides V2O5, NiO, Cr2O3, Fe3O4, Cu2O, MnO2, Pb3O4, SnO2, ZnO, and SiO2 act as inhibitors at the aluminum (Al) electrode.

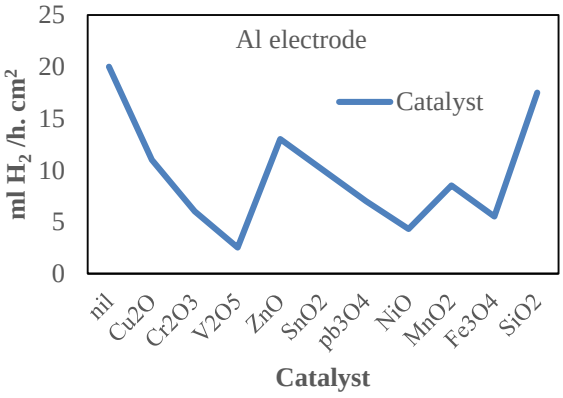


Fig.13.The effect of metal oxides at Al electrode.

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Fig. 14 demonstrates that the metal oxides V2O5, Cu2O, Cr2O3, and SiO2 act as inhibitors at the zinc (Zn) electrode. Conversely, ZnO, SnO2, Fe3O4, Pb3O4, NiO, and MnO2 serve as good catalysts for the production of GH.

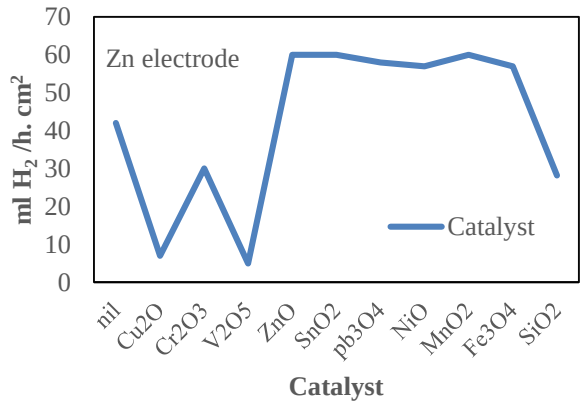


Fig.14. The effect of metal oxides at Zn electrode.

Fig. 15 illustrates that the metal oxides Pb3O4, Fe3O4, ZnO, Cu2O, Cr2O3, and SiO2 act as inhibitors at the lead (Pb) electrode. Conversely, SiO2, SnO2, V2O5, NiO, and MnO2 serve as good catalysts for the production of GH.

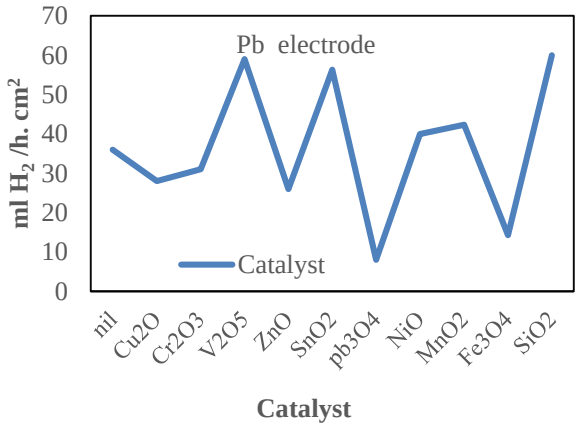


Fig.15. The effect of metal oxides at Pb electrode.

4. CONCLUSION

It was possible to produce GH in quantities exceeding normal production from seawater using zinc and lead electrodes in the presence of catalysts, such as oxides of ZnO, SnO2, pb3O4, NiO, MnO2 and Fe3O4at the zinc electrode, as well as oxides of V2O5, SnO2 and SiO2 at Pb electrode. They showed an increase in H2 production.

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