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MG-AL LAYERED DOUBLE HYDROXIDE CATALYST FOR GREEN HYDROGEN PRODUCTION

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ABSTRACT: Hydrogen production from water electrolysis has become a potential technology for replacing non-renewable exhaustible energy resources. The utilization of low cost, bifunctional catalysts and renewable energy sources for the electrolysis of water help to reduce the energy consumption and produce a high yield of green hydrogen (H2). This research paper describes the facile synthesis of Mg-Al Layered Double Hydroxide (LDH) electro-catalyst through the hydrothermal method for green H2 generation. The phase identification of crystalline material has been analyzed by using the X-ray diffraction (XRD) technique, whereas the surface area of synthesized LDH electrocatalyst was determined by using BET experimental data. The surface morphological structure of LDH catalyst was observed by using SEM images. From the electrochemical measurement data it was found that the synthesized electrocatalyst possess a cathodic current density of 10 mA/cm2 at 1.987 V and anodic current density of 10 mA/cm2 at 1.378 V and low Tafel slope which indicates the good electrochemical stability of Mg-Al LDH in basic medium. The synthesized electro-catalyst can be further use for the development of alkaline electrolyzer in order to produce the green hydrogen at larger scale.

KEYWORDS

Layered double hydroxide, Green hydrogen, Hydrothermal method, Corrosion

1. Introduction

The global energy demand has been increasing due to the scarcity of fossil fuels and environmental pollution concerns, so an alternative energy source has to be found to tackle the modern issues (Kuchkaev et al., 2021). The prominent and effective technology to replace the existing technology is electrolysis of water for producing hydrogen and oxygen fuels. Hydrogen has many advantageous features like highest gravimetric energy density, most efficient, clean and flexible source for almost zero carbon emissions (Srivastava, n.d.). This fuel doesn't liberate any harmful gases while combusting, so it is considered as a green fuel (Bhavanari et al., 2021). However, the hydrogen generation from water electrolysis is mainly governed by the hydrogen evolution (HER) and oxygen evolution reaction (OER) reaction steps. The efficiency of electrolysis is limited by certain factors like slow kinetics of HER and OER, long term stability, large energy consumption (Pandey et al., 2019).

An efficient electrocatalysts are necessary to enhance the reaction kinetics, stability of the electrolyzer system and also reduce the energy requirements by many folds (Bouali et al., 2020). There are some noble metal based catalysts which have better performance for HER and OER, such as Platinum based catalysts for only HER and iridium and ruthenium based oxides are considered as benchmark for OER activity enhancement(Kumar, Srivastava, & Chattopadhyay, 2021; Nouseen et al., 2021). Recent developments for efficient electrocatalysts include metal hydroxides/oxides, metal phosphates for OER activity in acidic medium, whereas metal alloys, metal chalcogenides, metal carbides/nitrides towards HER activity in acidic medium(Kumar, Srivastava, Pak, et al., 2021; Srivastava et al., 2021). There are some limitations for noble metal based catalysts for industrial adaptability like high cost, less availability, so developing a catalyst that can improve both the HER and OER activity and acts as bifunctional electrocatalysts(Chattopadhyay et al., 2020; Srivastava et al., 2020).

Recently Layered double hydroxides has gained major attention of researchers for their development and applications in various domains such as adsorption, electrochemistry, biomedical sciences, photocatalysis(Shanker et al., 2021). LDH are a class of layered anionic clays with a structural formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)^{A?}_{2}]\ A^{x}+ [A_{n}^{-}]_{x/n}\cdot mH_2O$, where M^{2+} (e.g., Mg^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} etc.) and M^{3+} (e.g., Al^{3+}, Fe^{3+}, Ga^{3+} etc.) represents the divalent and trivalent cations, respectively. A^{n-} indicates the interlayer gallery ions such as CO_3^{2-}, NO_3^{2-}, Cl^-, etc. along with water molecules (Feng et al., 2021; Shanker et al., 2021; Srinivasa et al., 2021; Yan et al., 2017). These LDH catalysts can be synthesized by using hydrothermal, co-precipitation, ion-exchange, sol-gel methods. The main objective of this paper to develop economically favorable LDH based bi-functional electro-catalyst for the development of alkaline electrolyzer.
In this manuscript, we have reported the synthesis of Mg-Al LDH electro-catalyst with nitrate ion present at interlayer gallery of metal oxide layers. This LDH can have better activity in different electrolytes and also helps to suppress the corrosion activity by trapping the corrosion responsible ions. The perimammary investigation of this research work suggest that the synthesized electro-catalyst can be used as bi-functional catalyst for the development of prototype alkaline electrolyzer to generate the green hydrogen from sea/tap water.

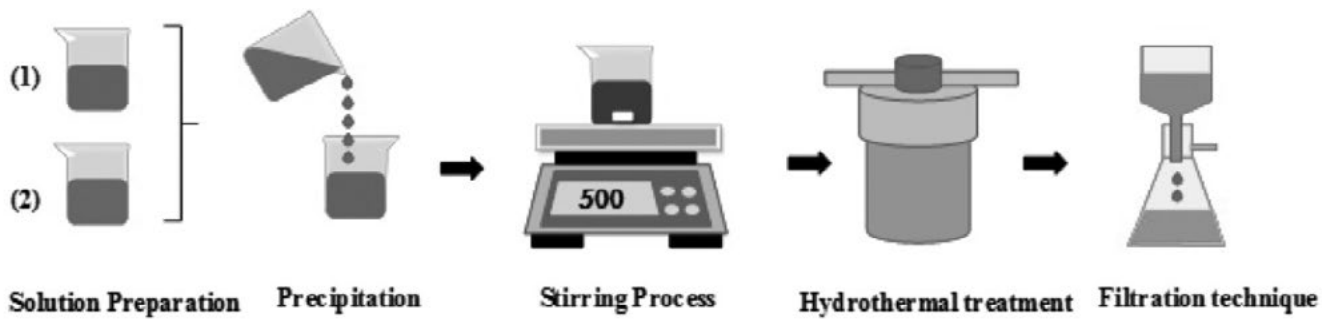
2. Experimental Procedure

2.1. Materials:

The essential chemical reagents such as Magnesium nitrate hexa hydrate (Mg $(NO_3)_2 . 6H_2O$), Aluminum nitrate nonahydrate (Al $(NO_3)_3 . 9H_2O$), Sodium nitrate ($NaNO_3$) and Sodium hydroxide (NaOH) were purchased from Merck, India Private limited.

2.2. Synthesis Procedure:

The synthesis procedure of Mg-Al–Nitrate 2D LDH electro-catalyst was prepared by hydrothermal method with slight modification (Zhang et al., 2021). Mg $(NO_3)_2 . 6H_2O$ (0.50M) and Al $(NO_3)_3 . 9H_2O$ (0.25M) was slowly added to 100 ml of $NaNO_3$ solution under vigorous stirring at room temperature. The pH of the solution was kept constant at 10-10.5 by simultaneous addition of NaOH solution (2.0M). The obtained slurry was introduced in to stainless steel autoclave for hydrothermal treatment at 65ºC for 24 hours. The obtained mixture was centrifuged (4800 rpm) and washed several times with distilled water.
The final product was dried at 50ºC temperature under atmospheric conditions for 12 hours. The entire step by step procedure for the synthesis of Mg-Al LDH electro catalyst is shown in Fig. 1.



(1) $Mg(NO_3)2.6H_2O$ and $Al(NO_3)_3.9H_2O$ (2) NaOH and $NaNO_3$

FIGURE 1: Schematic of Mg-Al –NO_3 LDH synthesis

2.3. Materials Characterization:

The physical characterizations and surface morphology of synthesized LDH electrocatalyst can be interpreted by using Scanning electron microscopy measurements (Model: Sigma 300, Zeiss). The crystallinity and lattice spacing of atoms in catalyst can be determined by performing X-ray diffraction experiments (Model No: D8 Advance, Bruker, Netherlands) in the 2θ range of 0º to 90º, whereas the intensity of diffracted x-rays was detected and analyzed by using standard intensity pattern of different compounds. The adsorption and desorption mechanism of nitrogen gas on synthesized LDH catalyst can be obtained by performing BET surface area analysis (micromeritics Tristar II 3020 3.02 instrument). The inert gas diffuses into the pores of the catalyst and adsorbed on the active sites, thus surface area and pore volume can be obtained according to BET theory assumptions.

2.4. Electrochemical Characterization:

The electrochemical techniques such as cyclic voltammetry, linear sweep voltammetry, tafel plot, electrochemical impedance spectroscopy describes the performance of catalyst in different electrolyte mediums. The voltammetry curves such as cyclic voltammetry and linear sweep voltammetry are obtained by varying potential at a particular scan rate in the definite potential range. The tafel plot suggests that amount of overpotential required for increasing the rate of electrochemical reaction, whereas the lower tafel slope indicates the better catalytic performance in an electrolyte medium. The electrochemical impedance spectroscopy measurements indicate the resistances for ion transfer towards electrode surface such as solution resistance, pore resistance, corrosion resistance, etc. All the electrochemical measurements were performed by using Gamry electrochemical work station (Model: Interface 1010). The electrochemical analysis of synthesized LDH electrocatalyst was performed in 3-electrode standard electrochemical cell as shown in Fig. 2.

3. Results and Discussion

3.1. X-ray Diffraction:

The Fig. 3 describes the X-ray incident diffraction pattern of synthesized Mg-Al LDH electrocatalyst. The constructive interface of monochromatic X-rays and sample is observed and the intensity is recorded with angle of incidence. The following miller indices of (012), (104), (110), (202), (119) matches with the standard data of magnesium oxide. The XRD pattern also indicates that synthesized LDH is crystalline in nature (Olfs et al., 2009).

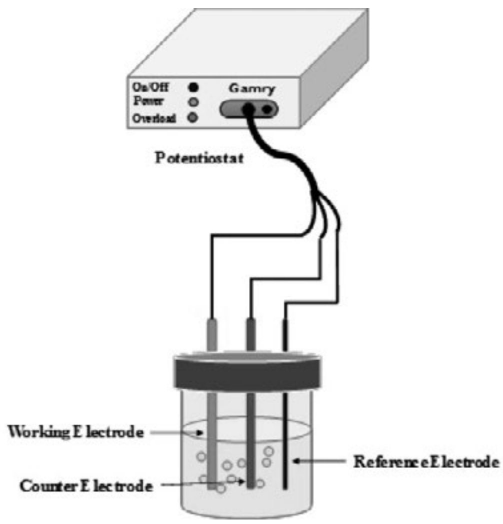


FIGURE 2: Schematic of electrochemical experimental set up

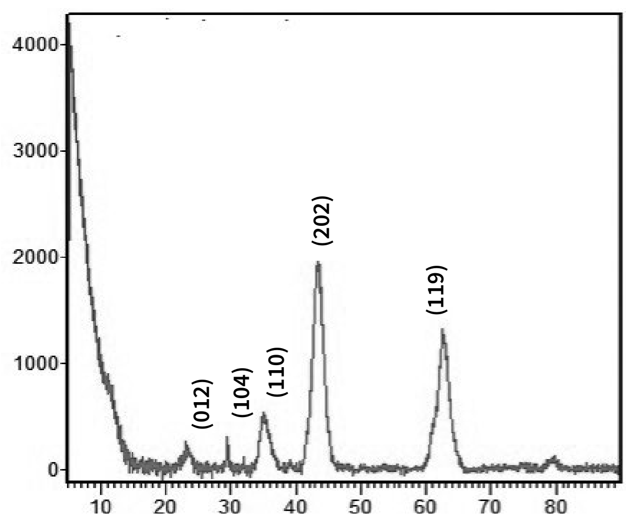


FIGURE 3: X-ray diffraction pattern of synthesized LDH particle

3.2. BET Surface area Analysis:

Fig. 4 gives information about adsorption and desorption pattern of N_2 gas on synthesized catalyst by the use of Brunauer-Emmett- Teller (BET) theory. This theory gives that synthesized electrocatalyst has surface area of 59.0055 m^2/gm. Barrett Joyner Halenda (BJH) desorption cumulative surface area of pores is 45.4229 m^2/g and single pore volume of 0.6854 cm^3/g respectively. The adsorption molecules are effectively desorbed by reduction in pressure, indicates that the reversibility of adsorbed molecules, thus Mg-Al-LDH catalyst can be used for hydrogen storage applications.

3.3. SEM Images:

The SEM images of Mg-Al-LDH electroctaalyst is shown in Fig 4. The scanning electron microscopy (SEM) analysis was performed for better understanding of surface morphology of LDH particles at 1μm resolution and different magnification. These SEM images (Figure 5 (a) and (b)) revealed that LDH particles looks like two dimensional flakes like structure. Each LDH particle may have different number of layers with ions present between the layers.

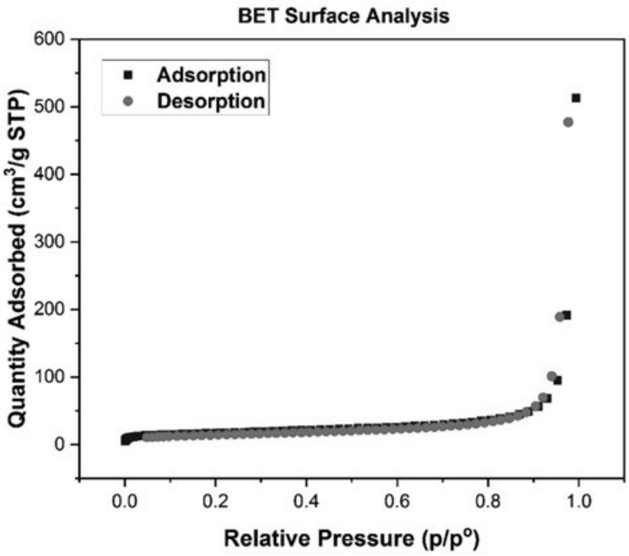


FIGURE 4: Adsorption and Desorption pattern of Mg-Al LDH

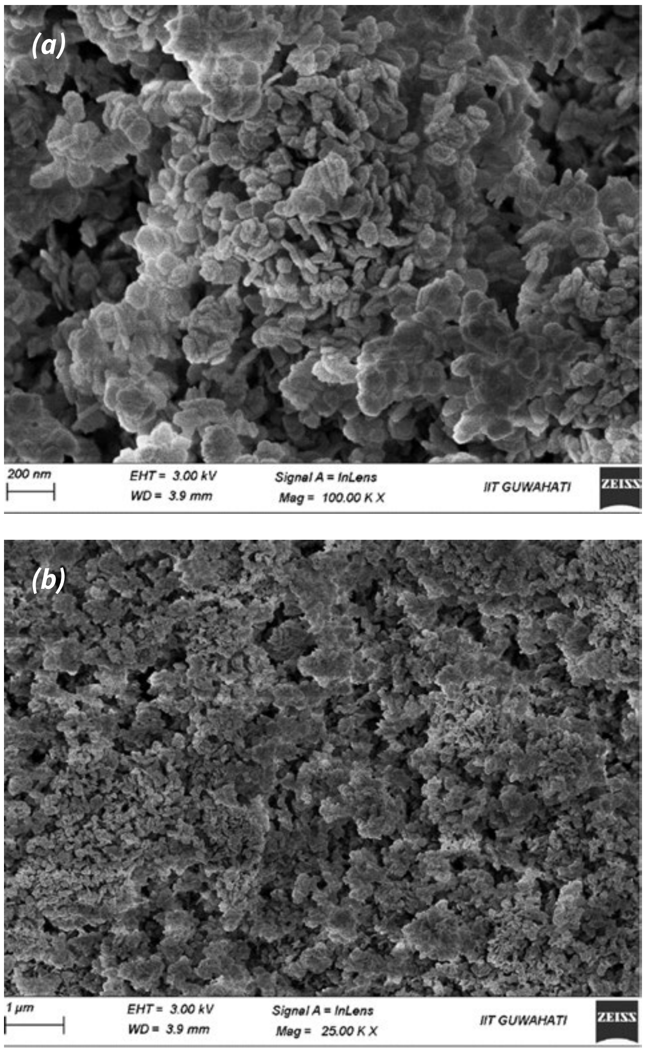
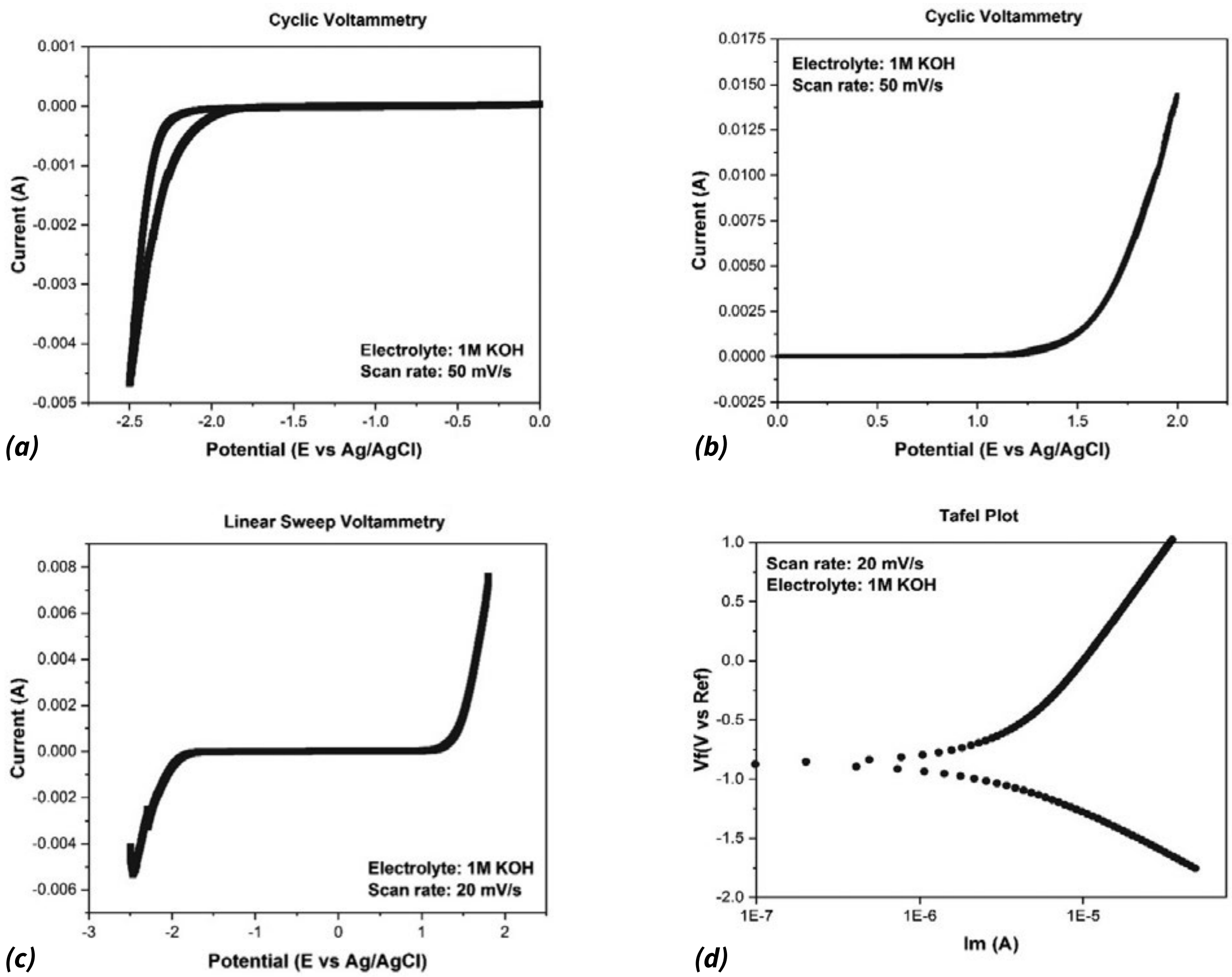


FIGURE 5: SEM images of Mg-Al LDH

3.4. Electrochemical performance of LDH:

The Fig. 5 represents the electrochemical performance of Mg-Al LDH electrocatalyst in basic medium (1M KOH). The figure 6 (a), (b), (c) of voltammetry curves illustrates that the catalyst possesses a cathodic current density of 10 mA/cm^2 at 1.987 V and anodic current density of 10mA/cm^2 at potential of 1.376 V. The figure 6 (d), (e) are tafel plot and impedance spectroscopy shows that the catalyst has better stability in basic medium. The lower tafel slope and high solution resistance implies that good electrochemical performance.



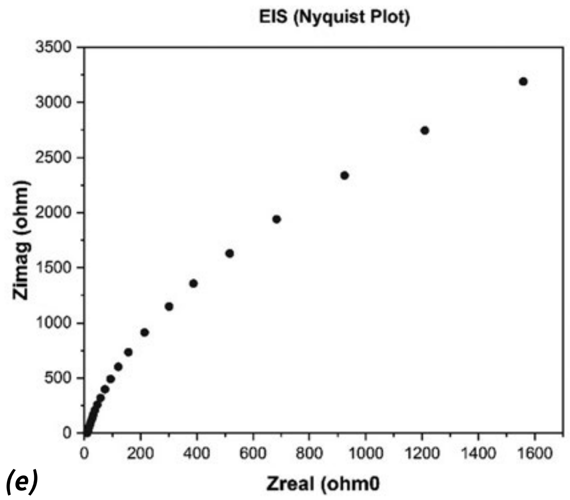


FIGURE 5: Electrochemical performance of Mg-Al-NO_3- catalyst in basic medium (a) Cyclic Voltammetry for HER, (b) Cyclic Voltammetry for OER, (c) Linear sweep Voltammetry, (d) Tafel plot, (e) Electro-chemcial impedance spectroscopy.

4. Summary

Mg-Al LDH electrocatalyst has been synthesized successfully with nitrate ion present at interlayer geometry of LDH and it is responsible for electrochemical and corrosion resistance applications. This synthesized LDH electrocatalyst has many advantages such as easy synthesis, good electrochemical performance, better stability and easy scale-up. The synthesized Mg-Al LDH electrocatalyst has been characterized with the help of various analytical instruments such as XRD, BET, SEM. The XRD data revealed that the synthesized catalyst has well defined crystal lattice structure. The BET surface area analysis shows high surface area around 59.0055 cm^2/gm , which can also reflects the hydrogen storage applications. The electrochemical performance analysis shows the synthesized electro-catalyst exhibits a cathodic current density of 10mA/cm^2 at 1.987 V potential and an anodic current density of 10mA/cm^2 at a potential of 1.376 V, which implies that LDH acts as bifunctional catalyst. The preliminary obtained data suggests that the synthesized electroctaalyst can be scale up to develop the efficient electrolyzer.

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