

**MORPHOLOGY - CONTROLLED SYNTHESIS OF ZINC
LAYERED DOUBLE HYDROXIDE FOR
ELECTROCATALYTIC CO₂ REDUCTION**

BY

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DHAHRAN, SAUDI ARABIA

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MASTER OF SCIENCE

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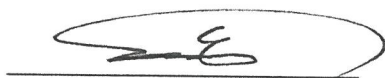
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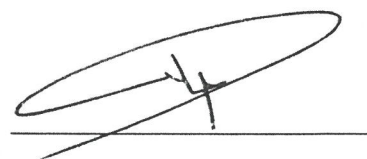
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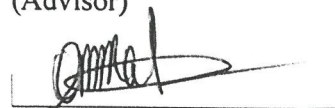
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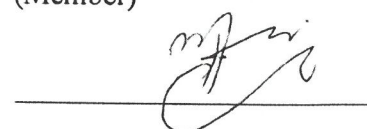
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This work is dedicated to those whose unwavering support and inspiration have fueled my academic journey. Their belief in my abilities and their encouragement in times of challenge have been the driving force behind the completion of this master's thesis.

*To my **family**, who have been a constant source of love and encouragement, thank you for your patience, understanding, and belief in my potential. Your unwavering support has been my anchor throughout this academic endeavor. To my thesis advisor, **Prof. Khalid R. Alhooshani**, whose guidance and expertise have been invaluable. Your dedication to the pursuit of knowledge and commitment to excellence have left an indelible mark on my academic and personal growth. To my friends and colleagues, thank you for the camaraderie, shared experiences, and the collaborative environment that made this academic journey more enriching and enjoyable. In the memory of **Mr. Mustapha Umar**, whose wisdom and encouragement remain etched in my heart. Your spirit continues to inspire and guide me, and this accomplishment is a tribute to your enduring influence. To all those who have played a role, big or small, in my academic pursuit, I extend my deepest gratitude. This achievement is as much yours as it is mine.*

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LIST OF ABBREVIATIONS

CO ₂	:	Carbon dioxide
GHGs	:	Greenhouse gases
IPCC	:	International Panel on Climate Change
CCU	:	CO ₂ -capture and utilization
CO ₂ -ECR	:	Electrochemical CO ₂ reduction
HER	:	Hydrogen evolution reaction
MOFs	:	Metal organic frameworks
Non-MHA	:	Nonmetal heteroatoms
EDL	:	Electrical double layer
IHL	:	Inner Helmholtz layer
OHL	:	Outer Helmholtz layer
GDE	:	Gas diffusion electrode
MD	:	Molecular dynamics
PDEs	:	Partial differential equations
SHE	:	Standard hydrogen electrode
CHE	:	Computational hydrogen electrode
CV	:	Cyclic voltammetry
LDHs	:	Layered double hydroxide materials
Zn-LDHs	:	Zinc-layered double hydroxides
LbL	:	Layer-by-Layer
UTFs	:	Ultrathin films
ZnPc	:	Zinc phthalocyanines
FLU	:	Fluorescein
SRB	:	Sulforhodamine B

ANS	:	Ammonium 1-anilinonaphthalene-8-sulfonate
BCZC	:	Benzocarbazole anions
DDS	:	Dodecyl sulfonate
AQS ²⁻	:	Bis (8-hydroxyquinolate-5-sulfonate) aluminum anion
PEDOT	:	Poly (3,4-ethylenedioxythiophene)
DI	:	Deionized water
RHE	:	Reverse hydrogen electrode
RR	:	Reaction Rate
TCD	:	Thermal conductivity detector
FID	:	Flame ionization detector
¹ H NMR	:	¹ H nuclear magnetic resonance spectroscopy
D ₂ O	:	Deuterium oxide
n	:	Number of electrons transferred during electrolysis
Z	:	The number of moles of products formed
F	:	Faraday's constant
Q	:	Amount of charge passed during the electrolysis in coulombs
FEG-SEM	:	Field Emission Gun Scanning Electron Microscopy
HRTEM	:	High-resolution Transmission Electron Microscopy
SAED	:	Selected area diffraction
XRD	:	X-ray diffraction
FTIR	:	Fourier-Transform Infrared Spectroscopy
XPS	:	X-ray Photoelectron Spectroscopy
EDS	:	Energy dispersive spectroscopy
SEM	:	Scanning Electron Microscopy
TEM	:	Transmission Electron Microscopy

ECSA : Electrochemical active surface area
Cdl : Double-layer capacitance

|

ABSTRACT

Full Name : Omer Ahmed Ali Taialla

Thesis Title : Morphology- Controlled Synthesis of Zinc Layered Double Hydroxide for Electrocatalytic CO₂ Reduction

Major Field : Analytical chemistry

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The anthropogenic carbon dioxide emissions has significantly and detrimentally affected our ecosystems. Electrochemical reduction (ECR) of CO₂ is one of the emerging alternatives to mitigate atmospheric CO₂ concentration and achieve a carbon-neutral state, primarily due to its capability to utilize renewable sources efficiently. However, the CO₂-ECR currently suffers from low efficiency and inadequate selectivity. Therefore, there is a pressing need for an efficient electrocatalyst that can enhance desired product selectivity and improve the process's efficiency. This work examined the elucidation of Zn-layered double hydroxides incorporated chlorine (ZnLDH-Cl) electrocatalytic CO₂-ECR activity. ZnLDH-Cl catalysts were synthesized, and CO₂ RR was performed using a CO₂-saturated KHCO₃ electrolyte to evaluate the electrocatalytic ability of ZnLDH-Cl catalysts. ZnLDHs intercalated with different species (Ca²⁺, Na⁺, and ⁺NH) were synthesized using metal chloride through hydrolysis process. The synthesized ZnLDH-Cl catalysts exhibited electrocatalytic CO₂-ECR activity for CO formation. The highest faradaic efficiency was achieved with ZnLDH-Cl/Ca demonstrating 99.7% at -0.96 V vs RHE with current density of 16.16 mA cm⁻² at a remarkably low overpotential of 0.436V. In addition, the catalyst maintains high stability in an aqueous medium and in terms of activity reaching up to 24. h.

ملخص الرسالة

الاسم الكامل: عمر احمد علي تاي الله

عنوان الرسالة: التخليق المتحكم فيه لهيدروكسيدات الزنك المزدوجة الطبقات من أجل الاختزال الكهروكيميائي الفائق لتقليل غاز ثاني أكسيد الكربون

التخصص: كيمياء تحليلية

تاريخ الدرجة العلمية: ديسمبر / 2023

إن الزيادة في انبعاث ثاني أكسيد الكربون البشري قد أثرت بشكل كبير وضار على نظمنا البيئية. الاختزال الكهروكيميائي لثاني أكسيد الكربون هو واحد من البدائل الناشئة لتخفيف تركيز ثاني أكسيد الكربون في الغلاف الجوي وتحقيق حالة محايدة للكربون وذلك بشكل رئيسي بسبب قدرة هذه الطريقة على استخدام مصادر الطاقة المتجددة بكفاءة. ومع ذلك، يعاني حاليًا من كفاءة منخفضة وانتقائية غير كافية. لذلك، هناك حاجة ملحة إلى عامل حفاز كهربائي فعال يمكنه تعزيز اختيارية النواتج المرغوبة وتحسين كفاءة العملية. في هذه الدراسة، تم دراسة النشاط الكهروكatalي لطبقة زنك المزدوجة المائنة المدرجة بالكlor ودرستها في الاختزال الالكتروكيميائي لغاز ثاني أكسيد الكربون باستخدام ثنائي كربونات البوتاسيوم المشبعة بغاز ثاني أكسيد الكربون ككهروليت لتقييم القدرة الكهروكatalيية للمحفزات على اختزال ثاني أكسيد الكربون الي مركبات اخري ذات فائدة أعلي وتأثير إيجابي على البيئة. تم تخليق المحفزات بثلاثة أنواع مختلفة من الهيدروكسيدات لدراسة تأثيرها أيضا على شكل المحفز الخارجي و اضافته كاتيونات مختلفة لزيادة كفاءته العامل الحفاز في اختزال ثاني أكسيد الكربون. أظهرت العوامل المحفزة المحضرة كفاءات مختلفة في اختزال ثاني أكسيد الكربون و اعلي كفاءته سجلت للعامل الحفاز المحضر عن طريق استخدام هيدروكسيد الكالسيوم حيث نجح في اختزال ثاني أكسيد الكربون الي اول أكسيد الكربون بنسبه تصل الي 99.7% مع فرق جهد منخفض بشكل ملحوظ عند جهد كهربائي يعادل 0.966 فولت مقابل قطب الهيدروجين القابل للعكس مع استقراره يصل الي 24 ساعة.

1. CHAPTER

INTRODUCTION

The global economy and societies rely primarily on fossil fuels like natural gas, coal, and petroleum for the generation of the major forms of energy needed in industrial activities and processes [1,2]. This reliance has led to a significant increase in atmospheric carbon dioxide (CO₂) concentration worldwide due to emissions [3]. Furthermore, it has contributed significantly to the acidification of water bodies, rising global temperatures, adverse weather conditions, and the devastating loss of important natural species [4–6]. These consequences have raised significant concerns due to the continuous increase in greenhouse gases (GHGs) produced by these processes. CO₂ is the major greenhouse gas that is promoting climate change due to anthropogenic human activities, among other sources, such as deforestation, cement production, and biomass burning [7]. Currently, the Earth's atmosphere holds about 412 ppm of CO₂, and it is increasing steadily. There has been an 11% increase since 2000 when the concentration was 370 ppm and a 47.5% increase since the beginning of the industrial period. The atmospheric CO₂ concentration was predicted by the International Panel on Climate Change (IPCC) to reach 950 ppm by 2100, inducing a 1.9°C average atmospheric temperature elevation [8,9]. To maintain the stability of our atmosphere and near region, it is of the utmost importance that this threat receives maximum mitigative attention like never before. Since fossil fuels will continue to play a significant role in the global supply of energy for an extended period, one way to reduce anthropogenic CO₂ emissions is to capture the greenhouse gas where it is produced. Although many adsorptive materials have been developed to accomplish this goal, the

vast majority of them have insufficient adsorption capacities and require high temperatures, as well as insufficient resources to permanently store the massive amounts of CO₂ released daily to annually [10–12]. Exploring and harnessing CO₂-capture and utilization (CCU) techniques provides a commercial avenue to convert CO₂ to value-added products to commensurate carbon management costs. Novel alternative techniques are currently being explored include thermochemical [13,14], electrochemical [15,16], plasma-based technology [17,18], biochemical [19], catalytic hydrogenation [20,21], and photochemical [22,23] **Figure 1**. Though these methods help in CO₂ conversion and consumption, they also have some limitations, such as restricted feedstocks (particularly for biochemical processes), low efficiency/selectivity, environmental impact of waste generated by their processes, catalyst instability or easy deactivation, high energy requirement (due to the inertia of CO₂), corrosion and degradation of materials (particularly for thermochemical processes), and so on.

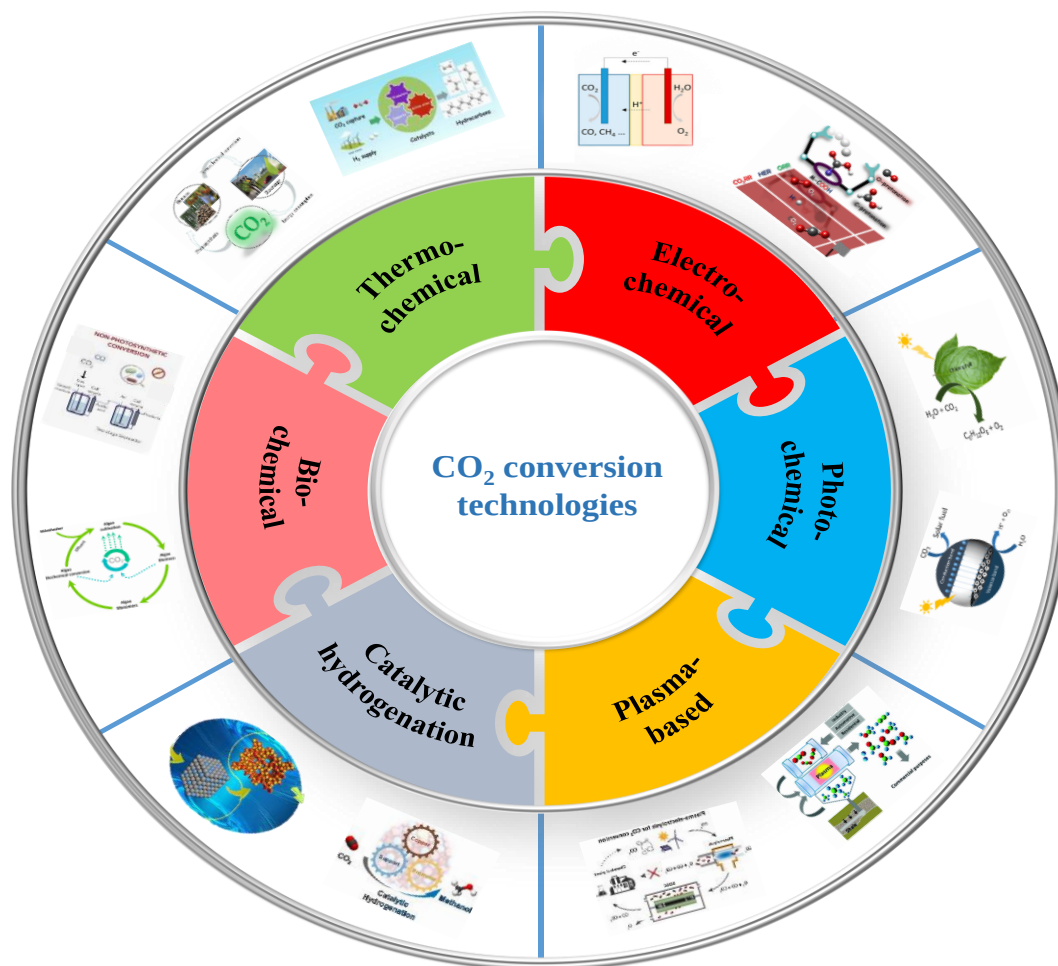


Figure 1: Various technologies of CO₂-capture and application (CCU) that offers an economic opportunity to transform CO₂ into value-added products.

Electrochemical technique offers a competitive advantage among others [24,25], such as the use of green and sustainable energy sources for the reduction of CO₂ to valuable products [26,27]; simplicity and ease of scaling up electrocatalysis systems, and mild and easily tunable reaction conditions. It also generates a wide range of industrial chemicals and useful fuels such as hydrocarbons (CH₄, C₂H₆), syngas (CO & H₂) formate, alcohols (CH₃OH, C₂H₅OH) in pure forms or as a mixture of products. Electrochemical CO₂ reduction (CO₂-ECR) techniques have achieved fascinating and intriguing accomplishments with numerous potential breakthroughs. However, it is pertinent to pay attention to some fundamental challenges of this technique which include high overpotential and limited solubility of carbon dioxide in the aqueous solution [28,29] formation of mixtures of product, thus necessitating expensive separation procedures [29,30]; catalytic deactivation of the electrodes by impurities, intermediates or wastes [28–30] The development of catalysts possessing high activities and selectivity [31,32]; and the competing hydrogen evolution reaction (HER) suppression are also included in them [33]. However, researchers have made significant progress in addressing some of the issues raised by developing electrocatalysts with exceptional characteristics. The numerous kinds of electrocatalytic materials studied so far, including, metal chalcogenides [34,35], metals nanomaterials [36,37], metal alloys [33], MXenes [38], metal-organic frameworks MOFs, carbon-based compounds [39], and metallic oxides [40–42].

CO₂-ECR has achieved fascinating accomplishments with numerous potential breakthroughs. However, it is pertinent to pay attention to some fundamental challenges of this technique which include but are not limited to: a) high overpotential

and low CO₂ solubility in the aqueous solution [43,44]; b) formation of mixtures of product, thus necessitating expensive separation procedures [44,45,29] c) catalytic deactivation of the electrodes by impurities, intermediates, or wastes [45]; d) development of catalysts possessing high activities and selectivity [31,32]; and e) the competing HER suppression [46]. However, researchers have made significant progress in addressing some of the issues raised by developing electrocatalysts with exceptional characteristics. The numerous kinds of electrocatalytic materials studied so far including, metal chalcogenides [34,47] metals nanomaterials [48,37]metal alloys[46], Mxenes [49], MOFs, carbon-based compounds [50], metallic oxides [51],[52],[53].

Metal oxides have emerged as promising electrocatalysts for the reduction of CO₂ to value-added chemicals and fuels. In this process, CO₂ is reduced to more useful molecules like carbon monoxide, formic acid (HCOOH), and methane (CH₄) using an electrochemical approach **Figure 2**. Metal oxides can act as efficient electrocatalysts due to their excellent electronic conductivity, stability under harsh conditions, and ability to tune their electronic properties by modifying their surface structure. So far, researchers have made significant contributions to morphological tailoring through careful preparation control of metal oxide structures [54], atomic-scale structuration [55], designing of electrolytes [56], and linking of crystallites [57]. The inorganic material-based heterogeneous electrocatalysts have demonstrated exceptional resilience during electrocatalytic tests. However, they undergo moderate to mild reconstruction in specific situations under the reaction conditions [58], This makes it

difficult to discuss the catalytic cycle operations without elucidating the operando technique.

H																	He
Li	Be	Hydrocarbons				Hydrogen				B	C	N	O	F	Ne		
Na	Mg	Carbon monoxide				Formate				Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Figure 2: The development of (carbon monoxide, Formic acid, Methane, and Methanol) byproducts over metal and metal oxide electrocatalysts. Copyright with permission from [59].

Nonmetal heteroatoms (Non-MHA) are expected to have more ability to alter the electronic structure of metal oxide catalysts than metal heteroatoms due to their significantly higher electronegativities (e.g., H, S, N, and halogens) [59]. Several post-treatment techniques, such as nitrogen plasma, are used to dope nonmetal components into metal oxide catalysts [60]. Also, wet-chemistry approaches, and post-annealing [61], have been established. However, the extra nonmetal doping method complicates the synthesis, limiting commercial-scale industrial manufacturing. Additionally, only superficial doping is feasible, where dopants are more prone to leach under cathodic potentials, lowering catalytic stability and diminishing the modifying effect. Catalysts with nonmetal doping, on the other hand, are more able to alter structure and composition under cathodic potentials during CO₂-ECR. As a result, to identify the true active sites and reaction

mechanism, it is critical to analyze the structure and chemical composition change during CO₂-ECR, which has sadly been overlooked by most prior nonmetal doping studies [62]. CO₂-ECR has solved specific problems and prepared the way for near-future sustainable technologies throughout the last two decades. Nonetheless, many challenges must be overcome to improve current density, minimize overpotential, and manage the stability and selectivity of carbon dioxide reduction over metallic/metal oxide electrocatalysts.

1.1 Fundamental of Electrochemical Reduction of CO₂-ECR

Reducing carbon dioxide into useful fuels and chemicals by CO₂-ECR is considered a promising and efficient approach. This process involves the use of an electrochemical cell and an applied voltage to convert CO₂ into various products at the cathode. Recently, this technology has gained more attention as a promising approach to reducing greenhouse gas emissions and addressing climate change [63–65]. The CO₂-ECR process is complex, but in essence, it involves the transfer of multiple electrons from an external electrical source to the cathode, which is usually a metallic electrode or a catalyst-coated electrode, in an aqueous medium. Proton transfer processes are also involved in converting CO₂ into value-added chemicals [66,67]. The thermodynamic reactions occurring during the CO₂-ECR process, and the corresponding redox potentials of the resulting products (both gases and liquids) are dependent on the reaction conditions and the catalyst used [67]. The catalyst's performance and selectivity in the CO₂-ECR process can be influenced by various crucial factors, including the electrolyte's pH, the type of electrode material, and the specific catalyst employed [68]. Also, the potential difference between the cathode and anode in the electrochemical cell is the major driving force behind the CO₂-ECR process [69]. The mass transfer of CO₂ to the electrode-electrolyte interface, which is required for aqueous-

phase CO₂ conversion, is also largely impacted by the CO₂ supply. Various factors such as electrolyte concentration, the form of electrodes, electrolyte pH, nature of the catalyst, membrane type, and CO₂ flow rate can affect this phenomenon, and thus have a significant impact on the CO₂-ECR activity [70]. The low mass transfer ratio of CO₂ is a major challenge in CO₂-ECR, as CO₂ is a gas and tends to have low concentrations on the surface of the electrode or electrocatalyst. This issue is further aggravated by the limited solubility of CO₂ in many electrolytes [70,71]. Several approaches have been employed in the recent past to improve mass transfer to overcome these challenges, including the use of electrochemical reactors, electrodes, electrocatalysts, and electrolytes. These approaches could potentially reduce reaction barriers to such an extent that reaction rates can be achieved at a sufficient level for CO₂-ECR [71,72]. Yue et al. [73] recently demonstrated an approach to enhance mass transfer and improve CO₂-ECR by introducing a hydrophobic surface, which lowers the water adsorption ability of the electrode. The transfer of dissolved CO₂ from the liquid electrolyte to the cathode-electrolyte interface is a key process in most CO₂-ECR electrochemical cells. This transfer is dependent on the gradual change in CO₂ concentration at the interface (as shown in [Figure 3](#)), The rate of transfer is influenced by several elements, such as the interfacial interaction area, total mass transfer parameters, and the total concentration driving force [68,74]. The quantity of gradients in the system depends on the solubility of carbon dioxide in the electrolyte, as well as the specified operational temperature and pressure of the electrolyzer cell. However, predicting these gradients in CO₂-ECR is a complex task because acid-base reactions such as CO₂ consumption by OH⁻ in the electrolyte can cause nonlinear deviations from Fick's law

behavior, resulting in reduced concentrations of CO_2 that are available to react at the surface of the electrode [68,75,76].

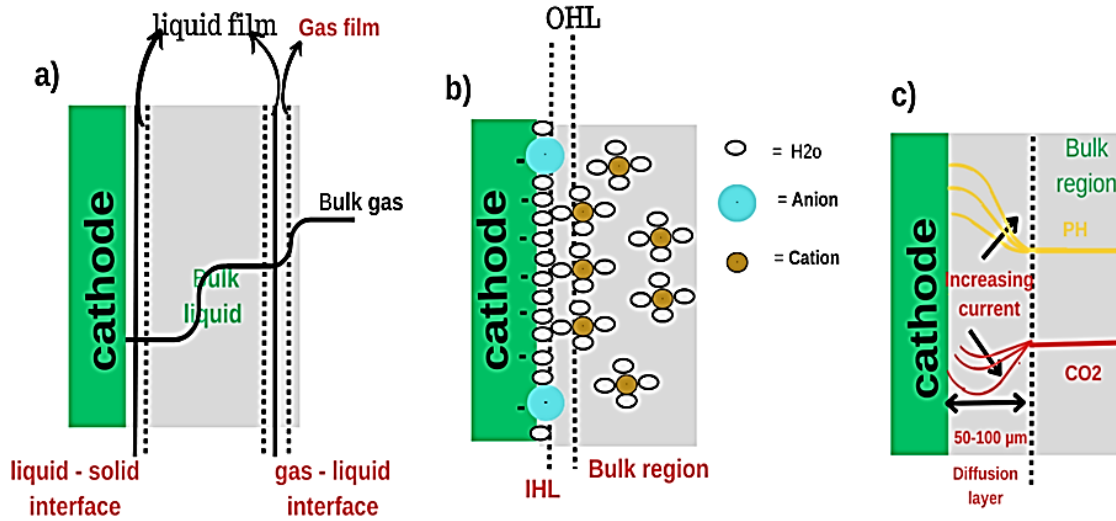


Figure 3: Illustrations of (a) the carbon dioxide concentration curve along gas, liquid, and solid interfaces. (b) The EDL with selectively adsorbed anions at the inner Helmholtz layer (IHL) & solvated cations at the outer Helmholtz layer (OHL), (c) Concentration gradient of CO_2 and pH close to the diffusion layer as j rises in a system with carbon dioxide supplied from the main electrolyte. taken from, with permission [68].

The impact of acid/base reactions in the electrolyte during CO_2 -ECR on concentration gradients can be mitigated by using buffering electrolytes like potassium carbonate (KHCO_3) to regulate the pH at the cathode [75]. To maximize the interfacial contact area, the size of the gas bubbles introduced to the electrolyte can be reduced or a 3D-structured electrode, such as a gas diffusion electrode (GDE), can be utilized [77–80]. Furthermore, GDE has been reported to be highly effective in providing a stable and

expanded three-phase boundary at the gas-liquid-solid interface, reducing the diffusion path of gas and enhancing mass transfer. As a result, it has been widely employed in CO₂ electrocatalysis due to its porous and electrically conductive composite coatings [81]. The mass transfer coefficients of CO₂ and CO₂-ECR products typically rise with temperature, pressure, and the velocities of gas and liquid in the electrolyzer but are also influenced by viscosity, the solubility characteristics of the electrolyte, and density. At the electrode-electrolyte interface, various phenomena such as charge transfer, phase transformation, and mass transport occur during CO₂-ECR. The electrical double layer (EDL), which describes the area of charge separation that arises at the interface between the electrode and electrolyte, is a fundamental concept in electrochemistry [82]. Having a thorough understanding of the events taking place within the EDL is essential for accurately modeling and predicting the reaction environment in electrochemical systems [83,84]. Besides that, the creation of the EDL is deemed critical in controlling both the kinetics of the CO₂-ECR reaction and the transportation of CO₂ molecules to the surface of the catalyst [85,86]. The EDL comprises two layers: the inner Helmholtz layer, which contains ions that bind tightly to the electrode surface, and the outer diffuse layer, which contains ions that are weakly adsorbed and are more mobile [83,87,88]. Several factors, such as the kind of electrode material, the concentration and type of electrolyte, and the applied potential, can influence the thickness of the EDL and the arrangement of ions within it [89]. The impact of these factors extends to the adsorption of CO₂ and other species onto the electrode surface, as well as the rate of charge transfer reactions that take place during the electrocatalytic process [90]. Apart from experimental investigations, a range of computational methods have been utilized to simulate the EDL and explore its influence on CO₂ electrocatalysis,

such as molecular dynamics (MD) simulations [91], density functional theory calculations [92], and continuum electrostatics models [93]. These models aid researchers in comprehending how the EDL behaves under varying conditions and forecasting how alterations in the system may affect reaction kinetics. For instance, Bohra et al. [86] they demonstrated the importance of the EDL and electrostatic attraction in determining the reaction conditions of CO₂ electrocatalysts. They observed a connection between the concentration of solvated cations and the increasing applied potential at the outer Helmholtz plane (OHP), while the pH in the initial 5 nm from the OHP was reduced due to the electric field in the EDL, resulting in an accumulation of protons and a corresponding reduction in OH⁻ ions. Similar attempts have been made by Le et al. [94] to summarize the recent developments in method development for modeling electrochemical interfaces. This work included various techniques for characterizing the electrolytes at the interfaces and diverse schemes for charging up the electrode surfaces, with particular attention given to the impact of pH and solutes like cations on electrocatalysis. In another development, Gupta et al. [76] employed partial differential equations (PDEs) to show that under typical experimental conditions, the local concentrations at the electrode surface differ considerably from the bulk concentrations.

The CO₂-ECR faces a significant hurdle in its commercialization due to its low energy efficiency, mainly caused by the CO₂-ECR high overpotential [95,96]. It typically defines overpotential as the gap between the reduction potential and the thermodynamic equilibrium potential at which the redox reaction occurs [97,98]. Overpotential is a well-known indicator of the demand for more energy than is strictly required by thermodynamics to initiate a reaction, which has an immediate impact on voltage efficiency

[99]. The sluggish kinetics required to form a CO_2^- intermediate is frequently cited as the source of overpotential in the CO_2 -ECR [100,101]. This step, which has a standard potential of -1.9 V versus standard hydrogen electrode (SHE), is the primary cause of the high overpotentials [99]. It has been found that one of the main functions of catalysts is to stabilize the intermediate, which can result in an improvement in the potential. Faraday efficiency is typically associated with energy losses. Even though all the current in CO_2 -ECR is used to produce products, the current that results in undesired reactions or products is usually counted as energy loss. The generation of H_2 is one primary unwanted product, which is produced due to the HER in the aqueous electrolyte [102]. From a commercial perspective, the primary market for CO_2 -ECR is fuel and commodity chemicals, which are currently dominated by oil-derived products. However, some CO_2 -ECR products, like CH_4 , may not be economically viable due to their competition with petrochemicals. Consequently, the formation of such products must be avoided, as the cost of electricity used to generate them may not be recovered [99].

1.2. Reaction Thermodynamics and Kinetics Insights of CO_2 -ECR

Recognizing the activity and selectivity of electrocatalysts relies on the reaction thermodynamics and kinetics [103]. Therefore, it is key to scrutinize the thermodynamic and kinetic details of different CO_2 -ECR catalysts. To be considered effective, a catalyst must diminish the activation energy barrier for reducing CO_2 compared to proton reduction, facilitate targeted CO_2 -ECR at minimal overpotential to enhance the energy efficiency, and furnish ample reaction sites for optimal reaction rates [104]. This can be reached by adjusting the energy of electrons with a biased potential to initiate the reaction. The

Computational hydrogen electrode (CHE) model is typically utilized to obtain the relatively straightforward thermodynamics of electrocatalytic reactions [105]. The immediate reduction of CO₂ entails a one-electron transfer process, forming the CO₂ anion radical (CO₂^{•-}). Nevertheless, the formal redox potential of -1.97 V versus SHE in an aprotic solvent (N, N'-dimethylformamide) and -1.90 V in water of pH 7, making this process extremely unfavorable. To mitigate the high energetic costs associated with the formation of CO₂^{•-}, catalytic strategies have been developed that utilize proton-assisted multiple-electron transfer to reduce CO₂. Reliant on the number of electrons and protons transferred, CO₂ can be reduced to produce 16 diverse products, such as CO, oxalic acid (H₂C₂O₄) (C₂O₄²⁻, basic medium), formic acid (HCOOH) (HCOO⁻, basic medium), formaldehyde, methanol, methane, ethylene, ethanol, ethane, and n-propanol [104,106]. The impact of various conditions on the CO₂-ECR reaction can be incorporated into the reaction scheme. Such conditions include the electrocatalyst properties (such as structure, dimensions or size, composition, oxidation state, and crystalline structure), electrolytes (concentration, anion, cation, and pH), pressure, applied potential, and temperature.

According to the thermodynamic relationship $\Delta G = -nFE^0$, where n is the number of electrons exchanged during the redox process while F is the Faraday constant, the reduction process with more significant positive E⁰ is preferable. Based on E⁰, the CO₂ reduction process to alcohol products or hydrocarbon might be more thermodynamically advantageous than CO, HCOOH, HCHO, and H₂ generation. Even though CH₃OH has a greater Gibbs free energy and poorer stability compared to CO₂ as shown in [Figure 4](#). Converting the highly unreactive CO₂ molecule into an energy-rich substance such as CH₃OH needs an external energy source, such as heat, irradiation/photons, or electrons

[63]. But this is not the case because of the presence of a thermodynamic barrier and the kinetic dependency of carbon dioxide reduction on the number of available protons in the solution. This suggests that the ideal catalyst should possess catalytic sites that are near proton donation sites, enabling efficient electron transfer. The formation of

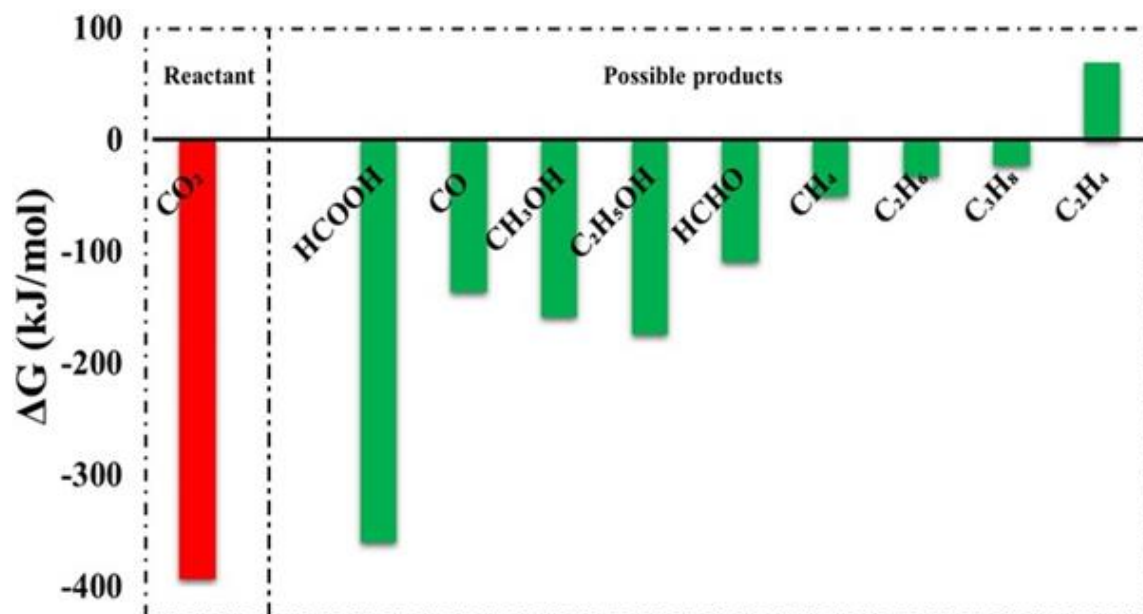
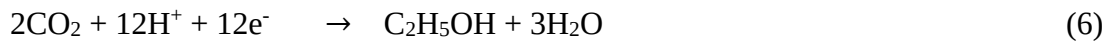


Figure 4: Chemical compounds with Gibbs free energies derived from the CO₂–ECR.

Adapted with permission from [64].

C–C bonds to produce C₂ and higher hydrocarbons is kinetically limited compared to the hydrogenation of adsorbed C1 intermediates, which affects the rate and selectivity of the reaction [107]. Several factors make it challenging to optimize electrocatalytic kinetics for CO₂–ECR, including the low solubility of CO₂ in water, low electrolyte pH and conductivity, and the requirement for an electrode structure that increases the number of reaction sites [108]. Some of these challenges have been addressed by recent developments in gas-phase systems, anion membranes [109], and hierarchical 3D electrode design

[110,111] Conversely, when a more negative potential is given to the aqueous electrolyte solution, the hydrogen evolution reaction (HER) begins to compete with the carbon dioxide electrochemical reduction (CO₂-ECR). The diminished faradaic efficiency can be attributed to the competition between CO₂-ECR and the HER, as both reactions take place within the same potential range [112]. The half-cell reduction potentials of CO₂ to the main products (listed below) are within +/- 0.2 V of HER.



1.3 Reaction Mechanisms of CO₂-ECR

To design CO₂-ECR catalysts that are highly efficient, it is essential to have a precise comprehension of reaction mechanisms. However, the generation of diverse products during CO₂-ECR makes its reaction mechanisms complex. Comprehending the reaction mechanism is crucial to designing and synthesizing of efficient electrocatalysts, as highlighted through both theoretical and experimental approaches [113]. In CO₂-ECR, the catalyst's capacity to preserve diverse reaction intermediates on its surface during the electrochemical process is largely responsible for the selectivity of the product. Numerous model catalysts have been examined to explore the likely reaction routes for generating

various products through CO₂-ECR [114–117] The CO₂-ECR products are usually determined by the amount of electron transfer. Pre-absorbed CO₂ is a critical element in the specific reaction pathways for CO₂-ECR. According to the qualitative molecular orbital theory, the molecule CO₂ has Lewis's basic character on its oxygen atoms and Lewis's acid character on its carbon atom, making it an amphoteric molecule. Despite the weak nucleophilic nature of the oxygen atom in CO₂, the electrophilic nature of the carbon atom is dominant because it has a somewhat negative electron affinity of around 0.6 eV and a first ionization potential of 13.8 eV. It has been observed that the two main ways of activating CO₂ molecules are coordination and insertion into metal centers, respectively [118,119]. In metal-aided activation, carbon-metal and oxygen-metal interactions bind CO₂ to the metal core. The characteristics and quantity of metal sites determine the variations in these interactions. When there is only one metal site, four distinct ways in which CO₂ might interact with the metal center. However, a variety of interaction types increases with additional metal sites, as demonstrated in [Figure 5](#). The nature of the metal itself, according to earlier research, determines the type of interaction between CO₂ and the metal core. Typically, metals with abundant electrons tend to prefer metal-carbon interactions, transferring electrons to the electrophilic carbon center's lowest unoccupied molecular orbital, consequently, leading to a bent structure of CO₂. In contrast, electron-deficient metal centers enable multiple forms of metal-oxygen interactions. On the other hand, the electron-rich oxygen atoms can at the same time interact with single- or double-metal centers using a monodentate or bidentate mode. In certain cases, the metal sites exhibit amphiphilic properties by interacting with both the LUMO of the carbon atom and the HOMO of the oxygen orbitals in CO₂; this simultaneous interaction leads to a bent

structure. These types of metal centers can donate and receive electrons to/from d-orbitals that are empty or filled, respectively.

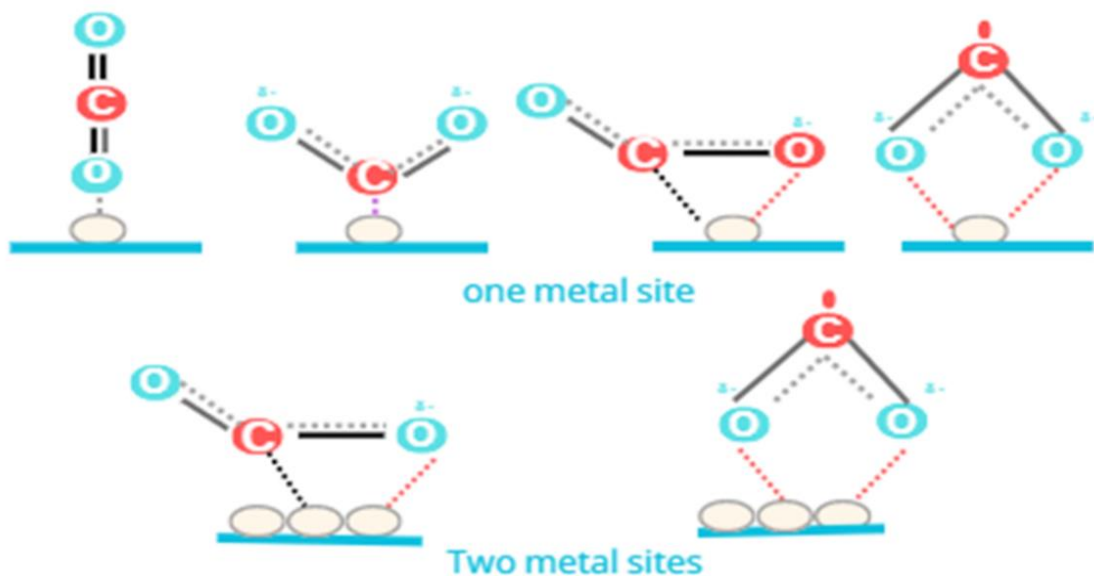


Figure 5: A possible number of modes of CO₂-metal interactions due to additional metals.

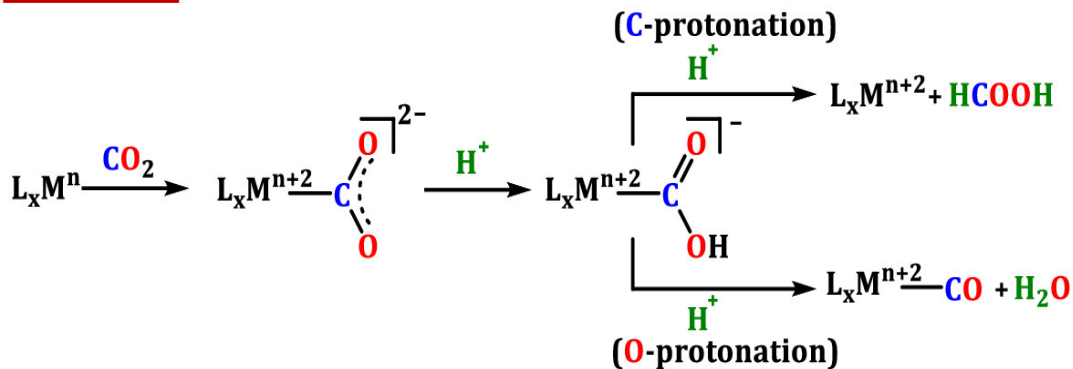
However, the activation of CO₂ through acid-base (metal-free) mechanisms can be achieved by utilizing a catalyst containing Lewis's acid-base sites. Meanwhile, the polarized nature of the CO₂ molecule arises from the higher electronegativity of oxygen atoms. As a result, the carbon atoms exhibit electrophilic behavior while the oxygen atoms act as nucleophilic centers.

Therefore, facilitates these atoms' ability to engage with the catalyst sites of the Lewis acid-base, resulting in the formation of CO₃²⁻ and HCO₃⁻ entities. Furthermore, in the presence of highly acidic centers, linear adsorption is preferred, whereas more basic centers lead to a bent structure. This bent structure facilitates the generation of activated CO²⁻ moieties due to electron transfer from the basic center [120]. These factors have an impact

on CO₂-ECR, where the electrophilic nature of the carbon atom prevails over the relatively weak nucleophilicity of the oxygen atoms. Most CO₂-ECR is reported to occur predominantly through two pathways: pathway I involves the binding of CO₂ to the catalyst's metal core. In contrast, the second consists in inserting CO₂ into a metal-hydride bond, as shown in [Figure 6](#). The first step in CO₂ activation in route (I) includes an electron-rich metal (nucleophilic) core attacking the electrophilic carbon center of CO₂. The HOMO of the CO₂ molecule is largely located on the more electronegative in nature oxygen atom, while the LUMO is a carbon-oxygen sigma antibonding orbital predominantly centered on the carbon atom. The LUMO is made up of a set of degenerate in-plane and out-of-plane C-O pi antibonding orbitals. Filling these sigma anti-bonding and pi anti-bonding orbitals with electrons obtained from the catalyst, primarily from metal-based orbitals, is required for CO₂ reduction. To achieve successful activation, the metal centers occupied by dz² and d_{xz/yz} orbitals must meet certain electrical structural requirements. There are numerous examples of complexes with a tetragonal ligand field and a d8 electron configuration, such as Fe⁰, Co^I, and Ni^{II} species. Nevertheless, catalytic activity can also be obtained by a complex with a half-filled dz² orbital, as demonstrated by species like Fe (I) and Co (II). The complexes of second and third transition metals might exhibit comparable behavior [118]. Kortliver et al. illustrated the likely reaction mechanism in molecular catalysts and transition metals for CO₂-ECR to various chemicals in [Figure 7](#) [121]. Cyclic voltammetry (CV) responses can be used to determine the CO₂ binding with the metal complexes and the binding constants. The rapid binding of CO₂ to metal during reduction induces a shift to the Faradaic response. In some cases, there may be no obvious change in the CV response in the presence of CO₂, which could be due to a lack of interaction between CO₂

and the reduced metal within the duration of the CV scan or in situations of minute binding to produce a significant effect [63].

Pathway I:



Pathway II:

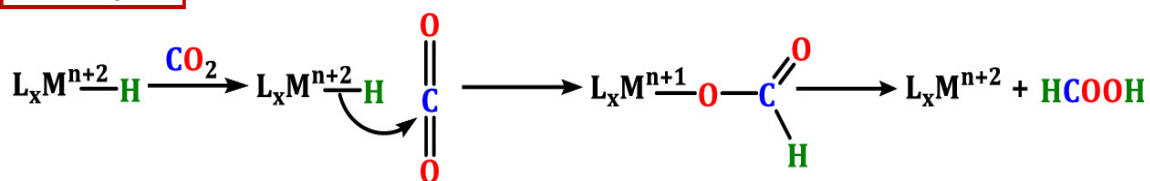


Figure 6: Possible CO₂-ECR routes to formic acid where: M = Metal, L = Ligand (ligand charge is not considered here), x = Stoichiometry of connected ligands, and n = Formal oxidation state of the metal. Adapted with permission from [122].

1.4 Research Objectives

The main objective of this research is to investigate the electrochemical reduction of CO_2 into value-added products using Zinc-layered double hydroxide chloride $\text{Zn}_x\text{O}_x(\text{OH})_2\text{Cl}_2$ as catalysts. The specific goals of the research are to:

- Synthesis of $\text{Zn}_x\text{O}_x(\text{OH})_2\text{Cl}_2$ with different hydroxide sources (amphoteric, e.g. Ammonia solution) and alkaline group (I) and (II) hydroxide, e.g. NaOH , $\text{Ca}(\text{OH})_2$.
- Characterization of the as-synthesize $\text{M}_x\text{O}_x(\text{OH})_2\text{Cl}_2$ catalyst.
- Electrochemical CO_2 evaluation.
- Electrochemical CO_2 characterization.

2. CHAPTER

LITERATURE REVIEW

Zinc-layered double hydroxides (Zn-LDHs) have recently enrolled as a focal point of scientific research, predominantly because of their unique attributes and extensive application potential [122]. These properties place them firmly within a special class of materials that has garnered increasing research attention [123]. Given the diverse applicability of Zn-LDHs, it is hardly surprising to find their influence permeating various scientific domains. These include, but are not limited to, areas like catalysis[124], medicinal drug delivery [125], environmental purification [126], and the formulation of nanocomposite materials [127]. The inherent flexibility in the layered structure of Zn-LDHs, combined with the modifiable chemical composition, creates promising avenues for material adaptation tailored to precise applications. Throughout this comprehensive review, special attention is dedicated to the diverse synthesis routes of Zn-LDHs. A detailed investigation into the characterization techniques offers insights into the methods preferred by researchers to study these materials in depth. Furthermore, a deep dive into the core principles that dictate the performance of Zn-LDHs promises to enhance our understanding of their operational efficiency.

2.1 The General Structure of Layered Double Hydroxide Materials (LDHs).

The fundamental architecture of layered double hydroxide materials (LDHs) is a critical starting point in comprehensively understanding this class of compounds [128]. LDHs are characterized by their layered structure, a feature of paramount importance that underscores their unique properties and diverse applications [129]. This elemental structure

consists of positively charged brucite-like layers comprising metal cations, which are interleaved with anionic species, typically in the form of hydroxide ions and exchangeable interlayer anions, as shown in **Figure 8**. The arrangement of these layers manifests in a repeated, planar fashion, forming a sandwich-like structure [130]. The propensity for LDHs to accommodate a wide variety of exchangeable interlayer anions is a distinguishing feature that has substantial implications for their functionality and applications [131]. The anionic species within the interlayer region are held in place by electrostatic interactions with the positively charged layers. This intercalation of anions contributes to the material's versatility and adaptability for various purposes.

LDHs occupy a unique niche within the realm of hydroxide ion conductors, a classification that isn't frequently encountered. Their prominence in this category stems from the profusion of hydroxyl groups intricately associated through covalent bonds within their two-dimensional host layer structure [132]. In addition to this, LDHs exhibit a meticulously structured channel [128]. This channel design displays a selective filtration mechanism, enabling the differentiation and separation of ions based on size [133]. Moreover, LDHs showcase an impressive hydrogen bond network [134]. This network is specially tailored for the efficient transport of hydroxide ions, further enhancing the material's conduciveness. Such a combination of attributes - the covalently bound hydroxyl groups, the selectivity of ion separation, and the robust hydrogen bond framework - not only underlines the versatility of LDHs but also magnifies their potential for a plethora of applications where ion conductivity and selectivity are paramount [129].

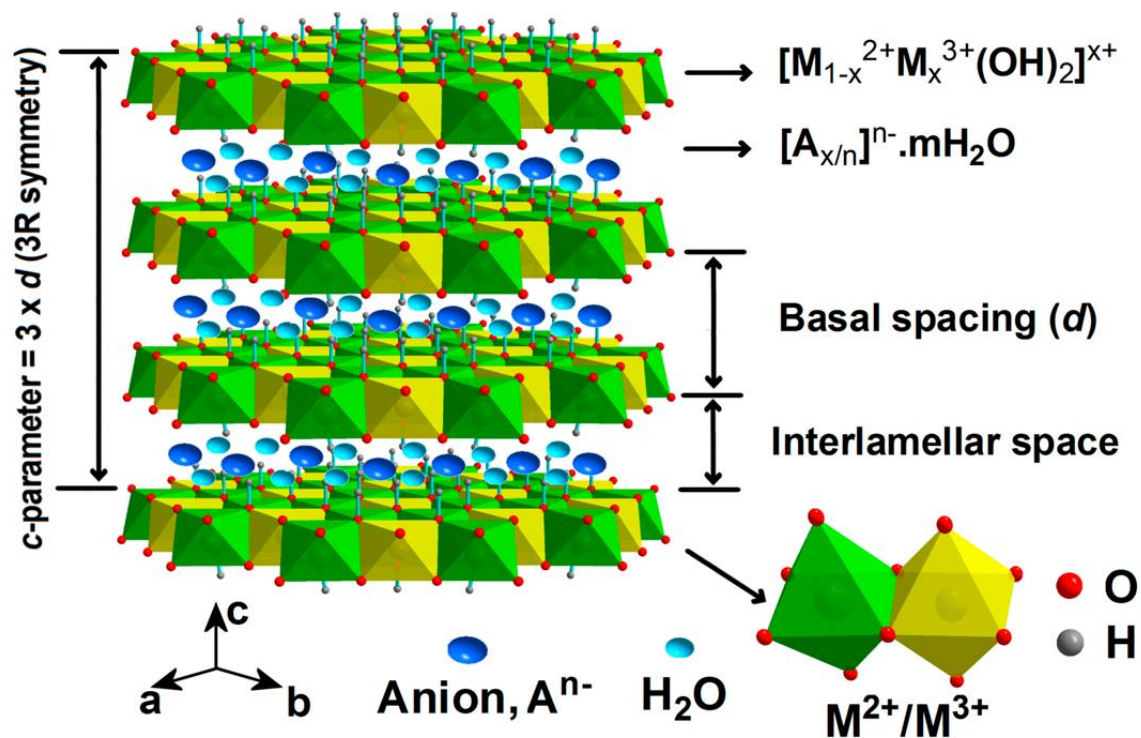


Figure 8: general structure of layered double hydroxide materials (LDHs).

Understanding the general structure of LDHs lays the foundation for exploring the synthesis, characterization, and myriad applications of these materials. Researchers often employ this knowledge as a starting point for the systematic design and engineering of LDHs, tailoring their properties to suit specific needs within diverse scientific and industrial contexts.

2.2 Preparation of LDHs

LDHs, owing to their diverse characteristics and applications, have attracted considerable attention in the realm of material science. The properties and morphological characteristics of LDHs largely depend upon the synthesis technique employed [135]. There are various techniques to synthesize these materials such as

2.2.1 Traditional Coprecipitation Method

The most widely adopted technique for preparing LDHs is the traditional coprecipitation method coupled with a subsequent hydrothermal treatment [136]. This method provides a consistent route for LDH synthesis, and its significance lies in the control it offers over the process parameters. Reactant concentration is the precise factor that researchers can control and tune to achieve the desired properties of the resulting LDHs [137]. Temperature Control: The temperature during synthesis plays a crucial function in determining the particle size and crystallization degree of LDHs [135]. By maintaining an optimum temperature, LDHs of desired morphological attributes can be achieved. Aging Time: Aging time, another influential parameter, when modified, can result in LDHs with varied particle sizes and crystallization degrees [138]. Through meticulous control over this factor, one can fabricate LDHs tailored for specific applications.

2.2.2 Alternative Synthesis Techniques

While the coprecipitation method remains dominant, various other techniques have been introduced to cater to the evolving demands for LDHs with specific properties such as In situ Growth: This method facilitates the growth of LDHs directly on a substrate, offering more control over the morphology of the resultant material [128]. Also, Electrosynthesis: Electrosynthesis allows the formation of LDHs by leveraging an external

electric field. This method provides an innovative avenue to modulate the properties of LDHs [139]. In addition, Calcination–Reconstruction: As the name suggests, this technique involves a two-step process where LDHs are first calcined and then reconstructed [140]. This process yields LDHs with specific morphological and structural attributes, as shown in **Figure 9**.

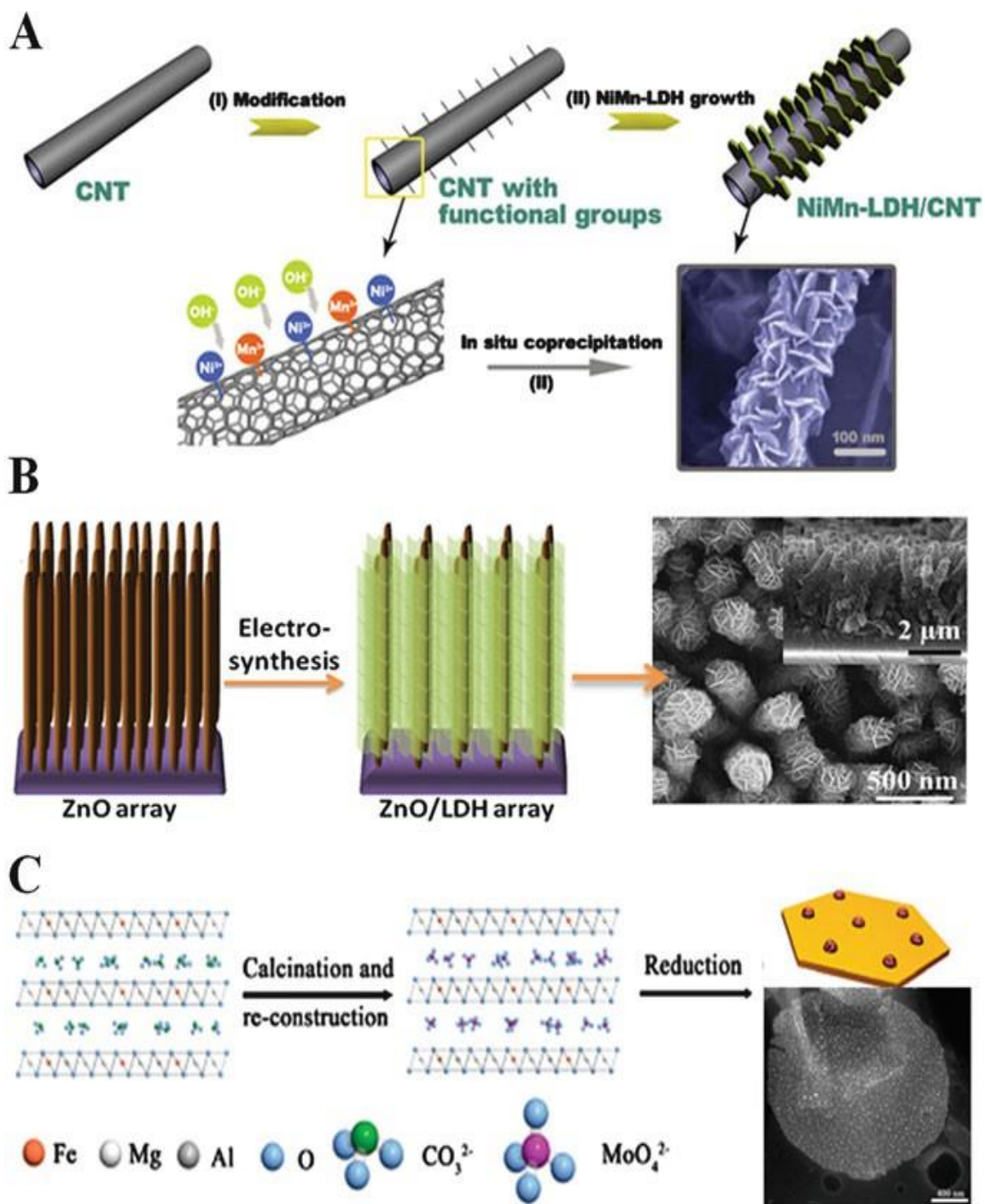


Figure 9: The LDH manufacturing processes include (a) in situ growth, (b) electrosynthesis, and (c) calcination-reconstruction (reprinted with approval from [140]).

2.3 LDH-Based Multifunctional Materials Fabrication

To produce multifunctional materials based on LDHs, guest species possessing diverse capabilities have been introduced into the interlayer galleries of LDHs. Additionally, LDHs with adjustable structure or morphology have been deliberately engineered [141]. The fabrication processes that are often utilized include the following.

2.3.1 Layer by layer Assembly (LbL)

The LbL technique capitalizes on the electrostatic interactions between the guest species and the LDH host. The fundamental Layer-by-Layer (LbL) technique is predicated on the sequential immersion of a substrate into a suspension containing LDH nanosheets with a positive charge, followed by a solution containing guest anions with a negative charge. A suggested approach for the co-assembling neutral molecules or positively charged ions as guest species involves the utilization of a polyanion carrier [142]. Additionally, using an external field, such as an electric or a magnetic field, might facilitate the production of ultrathin films (UTFs) that possess desirable characteristics like high guest loading, preferred orientation, and anisotropic features [143,144]. Therefore, the integration of guest anions with an LDH host enables the realization of a robust device with versatile functionality. Moreover, when positively charged LDH nanosheets plus negatively charged guest anions are present in a water-based environment, exfoliation-reassembly processes can be used to create LDHs that incorporate guests. This leads to the formation of nanohybrids exhibiting layered or core-shell, porous structures.

2.3.2 Intercalation Assembly

Intercalation assembly is a favorable option for the synthesis of multifunctional materials based on powdered or colloidal LDH, as stated in references [145] and [146]. The coprecipitation approach, followed by heat treatment, enables the attainment of direct intercalation. Co-intercalation is employed when there is a need to intercalate numerous guest species or if the guests are unable to directly fit into the LDH gallery [147,148]. In cases where the guest species exhibit instability in aqueous solutions containing divalent or trivalent metal cations, the utilization of ion-exchange techniques becomes feasible for the production of LDH-guest composites [149].

2.4 Application of LDHs

LDHs and composites based on LDHs have been extensively employed in many fields, such as photo-functional materials, catalysts, electrochemistry, and bio-related fields **Figure 10**. This is primarily attributed to their ability to have a customizable composition, a layered structure, and a contained microenvironment. This study aims to provide a comprehensive overview of the contemporary uses of LDHs and LDH-based materials. Additionally, we will explore the host-guest interactions and structure-function correlations associated with these materials [150,151,152,153].

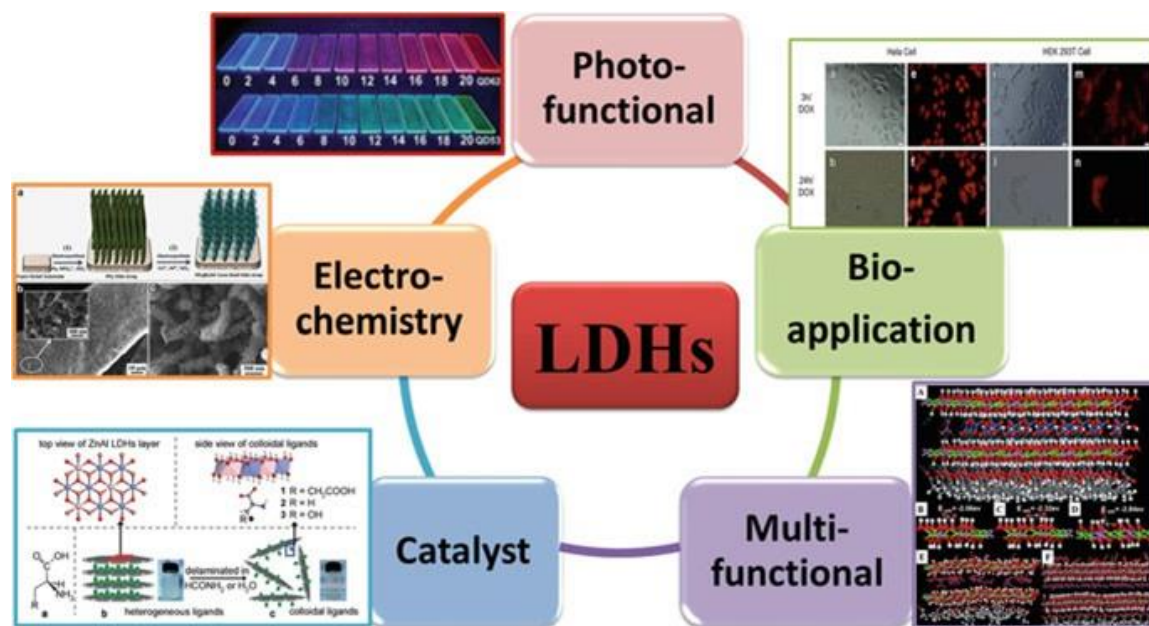


Figure 10: The utilization of Layered Double Hydroxides (LDHs) and materials derived from LDHs. reprinted with authorization from [151],[152],[153].

2.4.1 Photo-Functional Properties

LDHs have been widely used as photo-functional materials because of their layered structure, customizable composition, and impressive thermal and chemical resistance [154]. Luminescent LDHs exhibiting emission within the wavelength range of 350–550 nm may be synthesized by the presence of surface imperfections that effectively capture the excited electrons and holes, hence facilitating an augmented recombination process [155,156].

The process of incorporating and arranging fluorescent visitors into the interlayer galleries of LDHs is a commonly employed technique in many photo-functional applications. LDHs have been shown to accommodate a range of guest species, including organic fluorescent polymers [156], metal complexes [157], tiny anions [158], quantum dots [159], and

polyoxometalates [160,161]. Several approaches have been utilized to accommodate the diverse range of potential guest species. The various methods include LbL construction, co-assembly, direct intercalation (co-precipitation), ion exchange, & co-intercalation [162]. Therefore, by considering the interplay between the layers of LDH and the guest species, it is possible to adjust the arrangement and distribution of the guests that are intercalated between the layers [163]. By manipulating the chemical composition and the charge density of layers, it becomes possible to control the number of guest species, creating various characteristics. In addition, it is anticipated that the restricted habitat within the interlayer galleries of LDHs would impart unique performance and uses to the guest species.

2.4.2 Interaction of Host-Guest Between Guest Species and LDH Layers

The incorporation and insertion of photoactive guest species within the interlayer galleries of LDHs can impart improved fluorescence properties to the resultant LDH-based photo-functional materials. This enhancement is attributed to the interactions between the host LDHs and guest species, as well as the confinement effect exerted by the LDH structure. Through the process of co-intercalation, several guest species have been successfully included, including sulforhodamine B (SRB) [164] and zinc phthalocyanines (ZnPc) [165], fluorescein (FLU) [166], ammonium 1-anilinonaphthalene-8-sulfonate (ANS) [167], and benzocarbazole anions (BCZC) [168], have been successfully intercalated using surfactants as facilitators. One of the distinguishing features of these intercalation processes is the ability to manipulate the host layer composition and the ratio of intercalation. This fine-tuning enables the precise adjustment of the distribution and arrangement of the guest species within the structures. A direct consequence of this manipulation is the alteration of emission wavelengths and intensities, thus offering potential avenues for targeted luminescent applications.

Li et al. have delved deeper into this realm by co-intercalating bis (8-hydroxyquinolate-5-sulfonate) aluminum anion (AQS^{2-}) with dodecyl sulfonate (DDS) [169]. Their research has highlighted the potential of modifying fluorescence properties by varying the intercalation content and the host layer's composition. One significant finding from their work is the observed structural changes in the intercalated AQS. This change is not merely superficial, but rather, it is intrinsically tied to the host-guest interaction within the layered system. Furthermore, the luminescence transition observed in their study can be specifically linked to the isomerization of AQS, particularly from its meridional form to

the facial structure, as visually represented in Figure 1a. This transition further underscores the intricate relationship between the structural orientation of the intercalated species and their consequent luminescent outputs.

2.4.3 Application in Displaying and Sensing.

LDHs serve as a compelling basis for designing photo-functional materials. When the composition of guest species is carefully modulated within these structures, LDHs can be tailored to achieve a wide array of photo-functional materials. One of the notable benefits of introducing LDHs is the marked enhancement they impart to the fluorescence efficiency and longevity of the guest species contained within. Recent advancements have witnessed the emergence of innovative LDH composites. These composites, characterized by their bespoke arrangement within the LDH matrix, have applications in various domains. For instance, they have been integrated into display technologies [170,171], employed in polarized emission systems [140], and utilized for sensing purposes, as depicted in **Figure 11**. Further diversifying LDH-based luminescent materials; researchers have successfully achieved multicolor luminescence. This feat was accomplished by efficiently harnessing a broad spectrum of light-emitting entities, ranging from organic dyes and polymers to more complex structures [172]. Additionally, these LDH structures have also been instrumental in the realm of environmental and biochemical sensing. Materials designed for detecting heavy metal ions [173], biomolecular structures [174], and environmental contaminants [175] have been developed. Beyond these applications, LDHs have further been tailored to produce multifunctional materials. Such materials have

been designed to exhibit a response to variations in key environmental parameters such as pH levels [176], temperature [177], external pressure [178], and incident light [179].

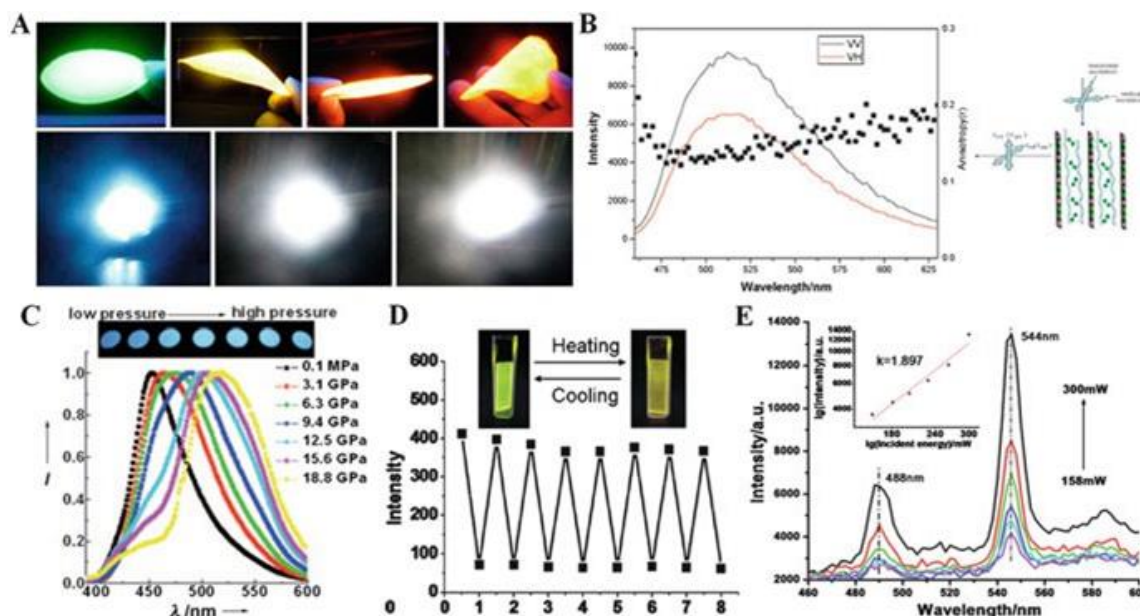


Figure 11: LDH-based photoactive materials for (a) screens, (b) polarized fluorescence, (c) piezochromic materials, (d) temperature monitoring, and (e) two-photon emission (adapted with permission from [179, 177,178].

2.4.4 Bio-Applications of LDHs

LDHs have recently emerged as a focal point in the realm of medical research, particularly in the context of their applications for developing innovative bio-inorganic nanohybrids. The unique two-dimensional structure of LDHs, combined with their intercalation capabilities, enables the creation of these novel nanohybrids [180]. LDHs possess a remarkable anionic exchange capability, which is a prominent characteristic of these materials, which facilitates the immobilization of a broad spectrum of biomolecules, ranging from pharmaceutical drugs and genes to vital nutrients, within their interlayer

galleries [125]. The fabrication of these intercalated nanohybrids is achieved through a diverse range of synthetic methods. Techniques such as exfoliation-reassembly, calcination-reconstruction, ion exchange, and co-precipitation have been employed with notable success. One of the primary applications of these synthesized nanohybrids is in the realm of bio-LDH delivery hybrid systems. These systems stand out for their ability to not only store but also transport and release bioactive species in a controlled manner [181]. The attributes of LDHs extend beyond their structural and intercalation characteristics. As materials, LDHs present many advantages, especially in drug and gene delivery, as well as broader biomedicine applications. Among their many benefits, such as Biocompatibility, LDHs are distinguished by their minimal cytotoxicity, making them optimal candidates for nanocarriers in drug delivery. Studies have revealed that LDHs display negligible cytotoxicity towards regular cells, with no observable cytotoxic effects at concentrations reaching up to 1 mg/mL [182]. Dispersion and Stability: When guest molecules are intercalated into the interlamellar galleries of LDHs, there's a marked enhancement in their dispersion and stability. Ease of Integration: The ability of LDHs to either intercalate or absorb various target materials – be it drugs, genes, proteins, nucleic acids, peptides, antibodies, or aptamers – negates the need for intricate ligand exchange reactions and additional surface modifications. Controlled Release: LDHs can be harnessed for the controlled release of intercalated drugs or genes, a property that's often pivotal for ensuring therapeutic effectiveness [183].

2.4.5 Applications in Catalysis

A. LDHs As a Catalyst

LDHs possess hydroxyl groups on their layers, leading to a significant number of basic sites within these compounds. This abundant basicity is a primary reason LDHs are highly effective as heterogeneous solid base catalysts [184]. Additionally, the inherent flexibility of the LDH structure allows for the anchoring of catalytically active transition metals within their host layers. Such integration enhances the catalytic activity and selectivity of the LDHs [185]. A diverse range of transition metals, including but not limited to iron (Fe), cobalt (Co), nickel (Ni), manganese (Mn), chromium (Cr), cerium (Ce), titanium (Ti), and copper (Cu), can be effectively incorporated within the LDH's host layer. The integration of these metals significantly amplifies the catalytic performance of LDHs across various processes, notably in electrocatalysis, photocatalysis, and photo-electrocatalysis [186].

Recent research endeavors have provided insights into the catalytic capabilities of LDHs. For example, Hu et al. examined the oxygen evolution reaction (OER) efficiency of NiFe and NiCo LDHs, comparing their performance before and after exfoliation. Their findings revealed that single-layer LDH nanosheets, post-exfoliation, showcased a marked improvement in catalytic activity relative to their unexfoliated counterparts. This enhanced performance was attributed to an increase in both the active site density and overall conductivity of the LDHs [187]. Comparable observations were made in the case of CoMn-LDHs [188].

B. LDHs as Precursor for Synthesis of Metal and Metal Oxide Catalysts

LDHs that include elements with catalytic activity, such as iron, cobalt, nickel, or palladium, have emerged as valuable precursors in metal or metal oxide catalyst fabrication. This process involves a calcination-reconstruction sequence, leading to the topological transformation of LDHs. Wei and his colleagues first introduced the concept of topological transformation in the context of LDHs, representing a significant advancement in the field [189]. Through this method, they successfully achieved the synthesis of high-density and well-dispersed metal nanoparticles, specifically Fe, Co, and Ni, while ensuring the preservation of their thermal stability. Notably, this transformation process offers an effective means of preventing the undesirable aggregation of these metal nanoparticles. For instance, in one notable study, He and his research team achieved the synthesis of nickel nanoparticles by employing an in situ reduction strategy utilizing a NiAl-LDH precursor [190]. The use of LDHs in this context proved to be instrumental in mitigating the aggregation of Ni nanoparticles. It induced a robust anchoring effect, thus facilitating the even distribution of the Ni nanoparticles. This research highlights the pivotal role of LDHs as precursors for the controlled synthesis of metal and metal oxide catalysts, offering enhanced stability and dispersion of catalytically active elements, such as Fe, Co, Ni, and Pd. Such advances in catalyst synthesis have broad implications for various catalytic applications.

C. LDHs Intercalated Hybrids as Catalysts

LDHs present a unique framework for the intercalation of catalytically active species within their interlayer galleries. The LDH structure provides intrinsic confinement, enabling precise control throughout the arrangement and distribution of the active species. Such control often culminates in augmented reaction rates and noteworthy catalytic stability. Moreover, with the modification of the density of charges and the compositional features of the primary layer, it is possible to enhance the control over both the geometric and electrical properties of the incorporated active sites. A diverse range of molecules and particles may be inserted into the LDH structure, including organic acids/bases, inorganic anions/nanoparticles, metal complexes, biomolecules, as well as noble metal nanoparticles [191,192,193]. This versatility leads to the creation of materials that showcase superior catalytic activity. As an illustrative example, a study by Hwang et al. delineated the formation of structured materials using a LbL assembly approach. They employed a ZnCr-LDH coupled with layered titanium oxide. The resultant heterolayer materials not only demonstrated impressive catalytic activity for O_2 generation when exposed to visible light but also maintained commendable chemical stability. Such studies underscore the significance of LDHs as a versatile platform for designing high-performance catalytic materials [194,195].

D. LDHs Intercalated Hybrids as Catalysts

To enhance the recyclability of catalysts, LDHs have been identified as effective stabilizers of active sites. Employing LDHs can lead to a high degree of dispersion in the immobilized catalyst particles [196]. Notably, metals such as gold (Au), palladium (Pd), and platinum (Pt) can be anchored onto LDH structures. This anchoring creates a synergistic interaction which, in turn, significantly amplifies the catalytic activity and selectivity, as represented in Figure 4d [197,198]. This advancement underscores the potential of LDHs in enhancing the performance and sustainability of catalysts in various applications.

E. LDHs in Electrochemistry

An enormous uptick in research into electrochemical energy storage and conversion methods has occurred throughout the last several years, driven by the imperative to seek sustainable alternatives to conventional energy resources [199]. To be more specific, progress in energy storage, such as supercapacitors, has necessitated the fulfillment of specific performance criteria, including high power density, an extended cycle life, and rapid dynamic response rates, to enable their broad utility [200,201]. LDH-based nanohybrids have emerged as promising materials for electrochemical applications, offering several distinct advantages. Firstly, the tunable composition of the LDH host layer enables the incorporation of electrically active transition metals like cobalt, manganese, iron, and nickel, thereby enhancing the electrochemical properties of these materials [202]. Secondly, various strategies can be harnessed to engineer LDH structures with extensive surface areas, well-suited mesopores, or ordered arrays, facilitating efficient electron

transport and, consequently, improving power density [203]. Thirdly, combining LDHs with various electrically active substances results in hybrid materials exhibiting long-term stability and expeditious redox reactions, thereby fulfilling crucial requirements for energy storage and conversion applications [204]. These features underscore the promise of LDH-based nanohybrids in the advancement of electrochemical systems with the potential for sustainable energy solutions.

F. The Composition and Structure of LDH-Based Electro Materials.

Recent advancements in the design and fabrication of electrically active materials have emphasized the development of diverse structural configurations, ranging from core-shell structures to layered arrays (as depicted in [Figure 12](#)). One particularly compelling illustration is the construction of a core-shell structure wherein poly (3,4-ethylenedioxythiophene) (PEDOT) is electrodeposited on an LDH nanoplatelet core, as showcased in Figure 5a [205]. The LDH core is responsible for a pronounced energy storage capacity within this configuration, while the enveloping PEDOT shell facilitates rapid electron transport.

In another innovative approach, NiAl-LDH microspheres with varying internal architectures, transitioning from core-shell to hollow structures, have been produced through LbL deposition complemented by an in-situ growth process (as highlighted in Fig. 5b) [206]. The hollow variant of these NiAl-LDH microspheres, with its ample surface area and mesoporous distribution, demonstrated a capacitance notably superior to its core-shell and yolk-shell counterparts. A similar conceptual approach was implemented using a carbon hollow sphere as the internal shell, while using NiAl-LDH for the outer layer,

yielding a material with an expansive specific surface area and a consistent mesoporous structure [207]. Moreover, the inherent porous nature of LDHs offers enhanced electroactivity [208]. Compositing these porous LDHs with conductive graphene nanosheets results in materials that exhibit significantly bolstered capacitance and exceptional rate performance capabilities, as illustrated in Fig. 5c [209]. Additionally, Fig. 5d presents a groundbreaking hierarchical nanoarray that involves vertically aligned NiCoFe-LDHs positioned on a Co-based nanowire array [210]. Such a material configuration indicates a high anodic current density coupled with robust electrochemical durability. Collectively, these advancements underscore the immense potential and versatility of LDH-based materials in electrochemical applications.

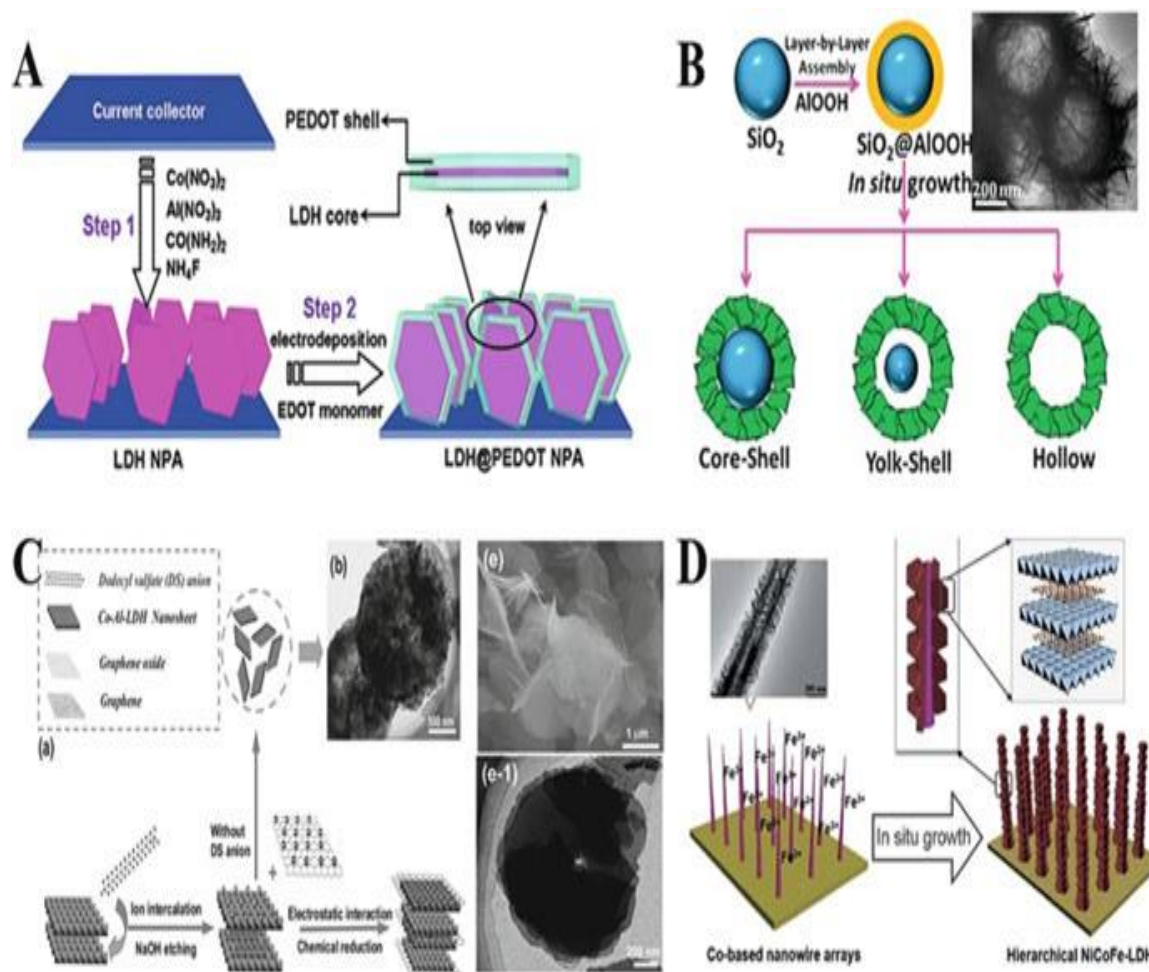


Figure 12: Electrically active materials with various architectures, including (a) core-shell structures, (b) hollow microspheres, (c) structures with multiple layers, and (d) arrays (reproduced with permission from [209, 206, 205].

Many studies have looked at the potential electrical activity of various LDHs with variable host layer compositions, as documented in the scientific literature [211,212,213,215]. In addition to these studies, researchers have sought to enhance the electrical performance of LDHs by incorporating carbon-based substances, conductive polymers, proteins, and metal oxides, among other auxiliary materials [140]. Among the materials examined for their

potential as electrically active components, carbon materials have garnered significant attention due to their inherent high electrical conductivity and cost-effectiveness [216]. For example, Zhao et al. conducted research to synthesize hierarchical nanostructures consisting of LDHs grafted onto a carbon material backbone via in situ growth methods [217]. These hybrid structures exhibited outstanding electrical activity and a noteworthy capacitance. Furthermore, graphene oxide and graphene have been employed with LDHs to create composite materials characterized by elevated catalytic activity and charge conductivity [218,140]. Beyond individual material investigations, novel applications have emerged from the synergy between LDHs and other substances. For example, Song et al. reported the fabrication of a high-rate asymmetric supercapacitor by amalgamating partially exfoliated graphite, CoNi-LDH, and polypyrrole (PPy) [219]. This innovative approach demonstrated superior electron/ion transportation capabilities and achieved a remarkable specific capacitance. The amalgamation of LDHs with diverse host layer compositions and supplementary materials has yielded a spectrum of electrically active materials, each offering unique properties and applications in the realm of energy storage and conversion. These research endeavors contribute to the expanding field of materials science and hold promise for future advancements in electrochemical technology.

3 CHAPTER

EXPERIMENTAL SECTION

3.1 Chemicals and Materials

Zinc chloride (ZnCl_2), deionized water (DI) filtered with TU 3+ Ultra-pure water system, sodium hydroxide (NaOH), Ammonium hydroxide (NH_4OH), Calcium hydroxide ($\text{Ca}(\text{OH})_2$), The product was acquired from Sigma–Aldrich. Unless explicitly stated differently, all precursors were used in their original form as received.

3.2 Synthesis of Catalysts

Synthesis of $\text{Zn}_3\text{O}(\text{OH})_2\text{Cl}_2/\text{Ca}$ (ZnLDH-Cl/Ca): ZnLDH-Cl/Ca catalysts were synthesized based on the reported method, facial hydrolysis method [Figure 13](#). In brief, 3g of ZnCl_2 was dissolved in 90 ml of deionized water (DI) under continuous stirring in an Ar environment (Ar was bubbled into the solution throughout the synthesis process). 1 M $\text{Ca}(\text{OH})_2$ solution was added into the solution dropwise. The pH of the solution was adjusted to 6.7. After stirring for 6 h at room temperature, the white precipitate was washed with DI several times and with ethanol two times. Finally, the dried powder was annealed at 180 °C for 1 h.

Synthesis of $\text{Zn}_3\text{O}(\text{OH})_2\text{Cl}_2/\text{Na}$ (ZnLDH-Cl/Na) & $\text{Zn}_3\text{O}(\text{OH})_2\text{Cl}_2/\text{NH}$ (ZnLDH-Cl/NH): The ZnLDH-Cl/Na and ZnLDH-Cl/NH were synthesized by the same procedure mentioned above but with a change of the source of hydroxide within the reaction vessel. One molar sodium hydroxide solution was used to synthesize ZnLDH-Cl/Na electrocatalyst. While one molar solution of ammonium hydroxide was used to prepare ZnLDH-Cl/NH.

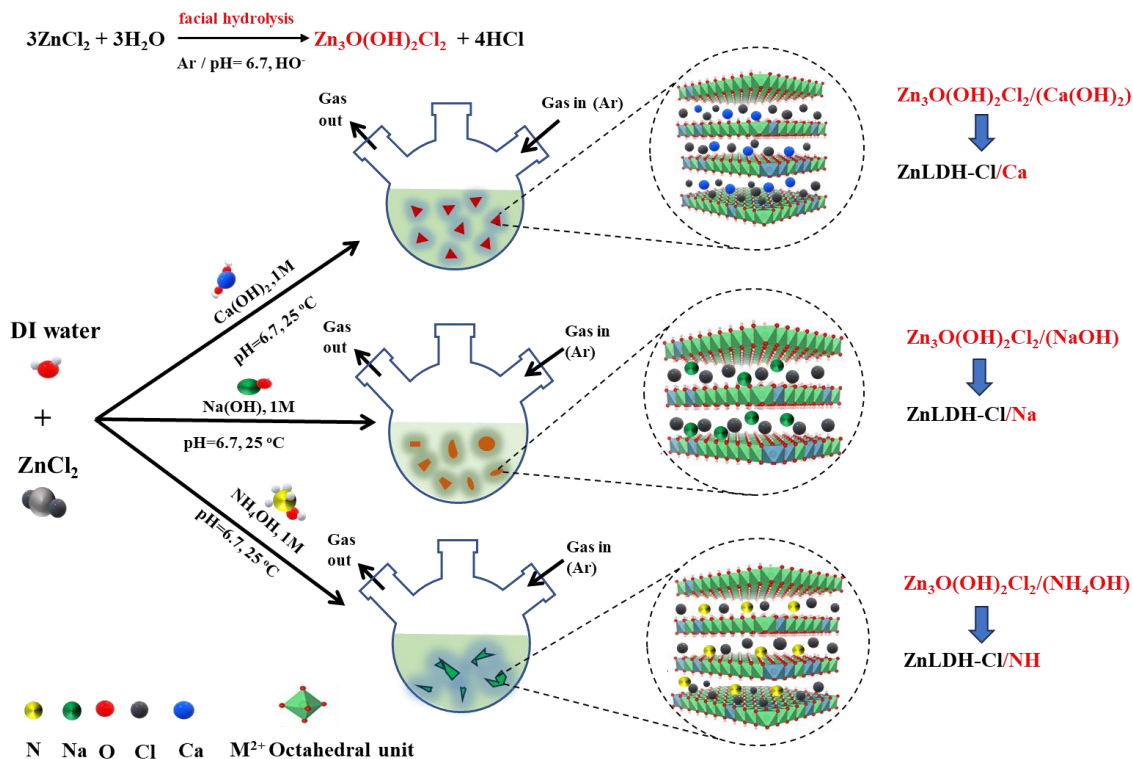


Figure 13: Schematic illustration of synthesis routes of the catalysts ZnLDH-Cl/Ca, ZnLDH-Cl/Na and ZnLDH-Cl/NH.

3.3 Electrochemical Measurements

The electrochemical investigations were carried out using a VersaSTAT3 apparatus (AMETEK, USA) equipped with a three-electrode system. The reference and counter electrodes comprised of Ag/AgCl in saturated KCl (ALS, Japan) and Pt wire (ALS, Japan), respectively. The working electrodes employed in the experiments were prepared with dimensions of $1 \times 1 \text{ cm}^2$. The CO_2 -ECR was executed within an H-cell (EC-frontier, Japan), employing a membrane separator (Nafion, N117) in a 0.5 M KHCO_3 electrolyte. To ensure the saturation of CO_2 in the electrolyte, high-purity CO_2 gas was introduced to the catholyte for a minimum duration of 30 minutes. The electrolyte maintained a pH of approximately 7.4. In this investigation, potential units were converted to the reverse hydrogen electrode (RHE) using the equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E^{\circ}_{\text{Ag/AgCl}} + (0.059 \times \text{pH})$$

Furthermore, a polarization curve was generated through linear sweep voltammetry (LSV) at a scan rate of 5 mV/s. The Reaction Rate (RR) was determined through chronoamperometry at various applied potentials within the range of -0.566 to -0.966 V (vs RHE). Throughout the reaction, the CO₂-ECR mixture was continuously purged with CO₂ gas at a flow rate of 5 mL min⁻¹ to maintain a controlled environment.

3.4 Products Analysis

The identification and quantification of gas products CO and H₂ were carried out using an online Clarus 580 GC (Perkin Elmer) instrument. The GC is equipped with Haysep and Molecular sieve columns, thermal conductivity (TCD) and flame ionization (FID) detectors. These columns and detectors are used to separate and identify the various components of the gas samples. The analysis was conducted under helium (He) and argon (Ar) carrier gases. Calibration of the Clarus 580 GC (Perkin Elmer) instrument was routinely performed using a standard gas mixture (GL Sciences, Japan) at 1 atmosphere. For sample analysis, injections were performed at intervals of 20 min through an automatic sampler. To ensure the removal of atmospheric contaminants from the tube line, the initial injection was initiated 500 seconds after running the CO₂-ECR process. All recorded measurements of the gas products were subjected to calculations to determine faradaic efficiencies [220]. This analytical methodology, utilizing state-of-the-art instrumentation and precise calibration techniques, was employed to accurately assess the efficiency of the electrochemical processes involved in the CO₂-ECR and quantify the yields of the specific gas products.

After 1 hour of continuous electrolysis, the electrolyte solution was collected and analyzed for the presence of alcohols and carboxylic acids. Additionally, the liquid products were analyzed using ¹H nuclear magnetic resonance spectroscopy (¹H NMR). To prepare for the ¹H NMR analysis, solutions were made that consisted of 86% electrolyte and 14% deuterium oxide (D₂O), along with internal standards of phenol and dimethylsulfoxide.

These solutions will be measured using a water suppression technique on a Bruker 400 MHz NMR spectrometer.

The efficiency of the products (both gas and liquid) will be evaluated using a specific equation known as the Faradaic efficiency equation (equation 2). The equation considers the number of electrons transferred during electrolysis (n), the number of moles of products formed (Z), Faraday's constant (F), and the amount of charge passed during the electrolysis in coulombs (Q).

$$f = \frac{Z n F}{Q} \times 100 \quad (2)$$

3.5 Characterization of As-Prepared Catalysts

The comprehensive characterization of catalytic materials aimed to elucidate their physical, chemical, and structural attributes. This detailed examination offers valuable insights into the diverse structural and chemical behaviors of the catalysts, fostering a deeper comprehension of the relationship between their structure, properties, and performance.

The phases and crystal structure of as-prepared catalysts were evaluated using X-ray diffraction (XRD), Rigaku Ultima IV diffractometer, operated at 40 kV and 40 mA with Cu-K α radiation ($\lambda = 0.154$ nm) between the scan range of 3° to 80°. For identifying and analyzing functional groups present in a sample, Fourier-Transform Infrared Spectroscopy (FTIR) was used in the scanning range from 500 to 4000 cm⁻¹. The morphology of as-synthesized catalysts was examined using Field Emission Scanning Electron Microscopy (FE-SEM). High-resolution Transmission Electron Microscopy (HRTEM), utilizing a Titan 80-300 microscope by FEI, was employed to observe both the morphology image and crystal structure information through the selected area

diffraction (SAED) patterns. The surface element composition was analyzed through a High-resolution X-ray Photoelectron Spectroscopy (XPS) instrument, utilizing monochromated aluminum Al K α (1486.4 eV) anode radiation at 72 W and 15 kV. Binding energies were calibrated using the Au 4f peak at 84.0 eV as a reference point.

4 CHAPTER

RESULTS, DISCUSSION AND CONCLUSION

4.1 X-ray diffraction Pattern (XRD) Analysis

The crystal structure of the ZnLDH-Cl/Ca, ZnLDH-Cl/Na and ZnLDH-Cl/NH were analyzed by XRD in the range of 2θ from 3° to 80° , as shown in [Figure 14](#). The diffraction peaks of ZnLDH-Cl/Ca and ZnLDH-Cl/Na are precisely matched with the zinc oxide pattern (JCPDS No. 80-0075), the characteristic peaks of zinc layered double hydroxide (LDH) (JCPDS No. 35-1575), the characteristic peaks of zinc chloride (JCPDS No. 39-0787) and some low-intensity peaks corresponding to zinc oxychloride (JCPDS No. 45-0819). The XRD analysis has elucidated the formation of zinc-layered double hydroxide (ZnLDH). The resulting XRD pattern is characterized by several distinctive peaks at specific 2θ angles, specifically at 10.86, 32.64, 32.74, and 37.66, indicating a robust crystalline structure. A notably intense peak at $2\theta = 15.44$ corresponds to the presence of the zinc chloride phase, underscoring the composition's crystalline nature. Additionally, a less intense peak manifests at $2\theta = 28.46$ and 44.56, revealing the existence of zinc oxychloride within the compound. Moreover, the 2θ range of 30 to 40 showcases more pronounced peaks, which can be attributed to the zinc oxide phase, further affirming the compound's chemical composition. Notably, the XRD patterns produced by the two distinct synthesis routes involving Ca(OH)_2 and NaOH, exhibit remarkable similarity in their profiles. However, a discernible distinction arises in the degree of crystallinity. In particular, the XRD pattern of ZnLDH-Cl/Ca exhibits a well-defined layered double hydroxide structure when compared to the other two catalysts. Conversely, the XRD pattern of ZnLDH-Cl/NH reveals a lower degree of crystallinity, characterized by a limited number of peaks indicative of the zinc-layered double hydroxide phases.

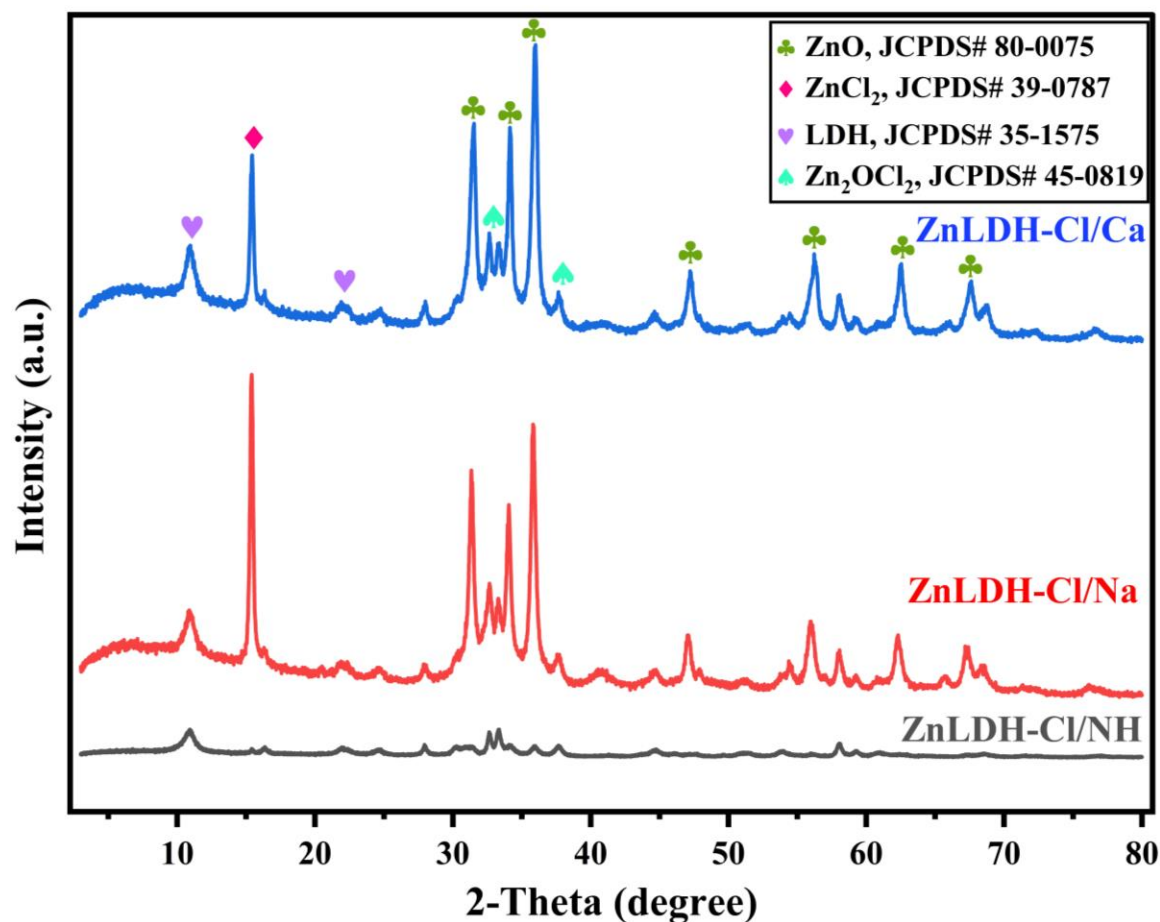


Figure 14: X-ray diffraction pattern of as synthesized catalyst ZnLDH-CI/Ca, ZnLDH-CI/Na and ZnLDH-CI/NH.

4.2 Fourier Transform Infra-Red Spectroscopy

FTIR spectra for the three prepared catalysts are illustrated in Figure 15. From this figure, it is clearly seen that both ZnLDH-CI/Ca and ZnLDH-CI/Na are showing broad vibration bands for O-H and/or interlayered water molecules stretching vibration at 3565.33 cm⁻¹ and 3561.24 cm⁻¹ respectively [221], Where ZnLDH-CI/NH showed a weak vibration band of high energy of 3560.51 cm⁻¹ assigned to N-H stretching vibration, the weak vibration of N-H band can be explained by low abundance of N-H in prepared catalysts as indicated by EDS results. ZnLDH-CI/Ca and ZnLDH-CI/Na are showing

common vibration band at about 1616-1619 cm^{-1} for hydroxyl O-H group and/or interlayered H_2O bending vibration [222]. Another common vibration band with high frequency observed at 2925.31 cm^{-1} and 2925.33 cm^{-1} shared by ZnLDH-Cl/Ca and ZnLDH-Cl/Na attributed to carbonate stretching vibration. Two vibration bands have been observed in all three catalysts with low frequencies below 1000 cm^{-1} to about 700 cm^{-1} such as 700, 878, 458.7, 697.48, 876.50, 703.40 and 879.72 cm^{-1} referred to Zn-OH and O-Zn-O stretching vibrations along with additional bands below 500 cm^{-1} includes 458.7, 475.59 and 461.83 cm^{-1} for ZnLDH-Cl/Ca, ZnLDH-Cl/Na and ZnLDH-Cl/NH respectively [223].

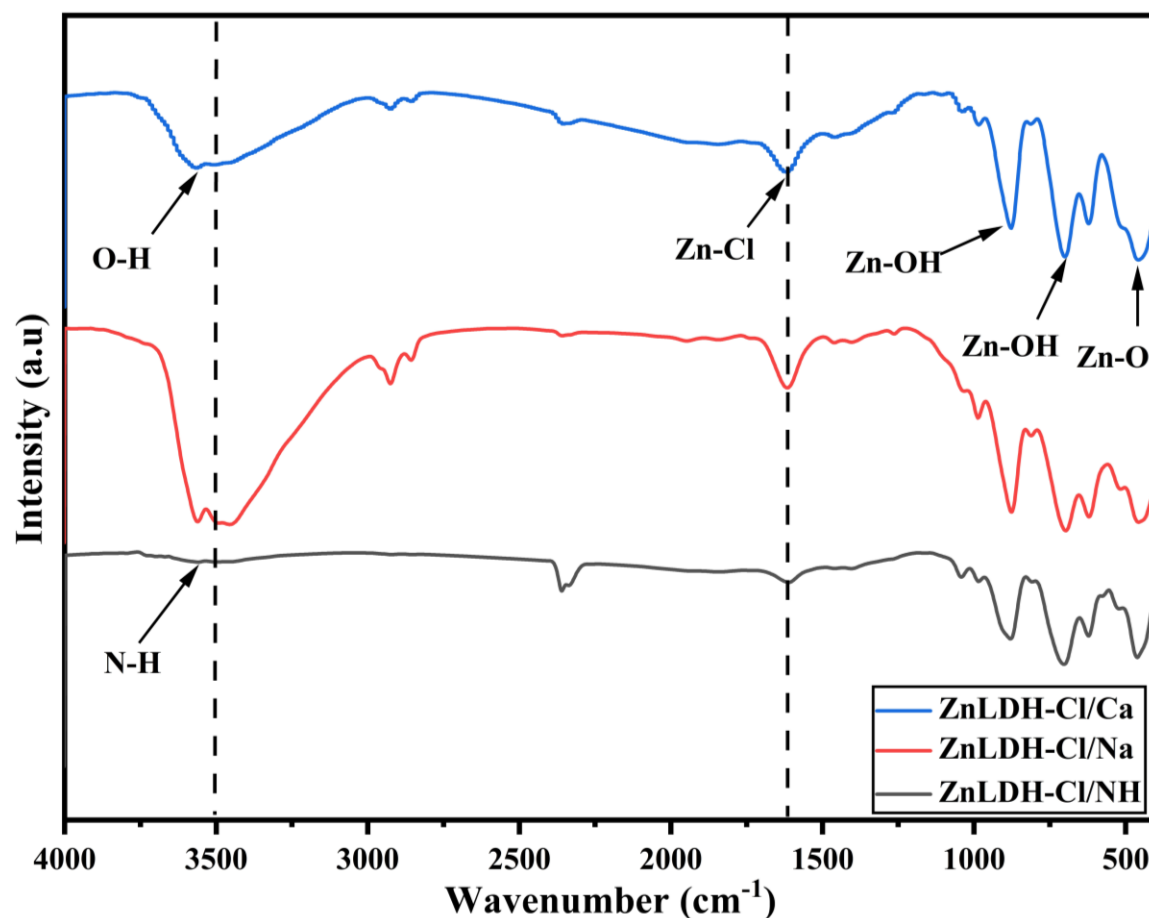


Figure 15: FTIR for ZnLDH-Cl/Ca, ZnLDH-Cl/Na and ZnLDH-Cl/NH.

4.3 Scanning Electron Microscopy and EDS Analysis

The three prepared catalysts' surface morphology has been studied using a scanning electron microscope. Figure 16 shows obtained micrographs of the surface scanning; a clear variation of catalysts surface morphology observed upon treatment with three different sources of hydroxide. Nano flakes with a thickness of about 79 nm are observed with ZnLDH-Cl/Ca catalyst Figure 16 a-c. The growth of these plates appears very homogenous and organized with almost similar size to the plates and abundant

sharp edges. EDS mapping [Figure 17](#), for this catalyst, showed even distribution of atoms among selected areas with dominant presence of Zn over oxygen, chloride and calcium. The second catalyst, which was prepared using sodium hydroxide base, showed poor growth of regular particles. Mostly appear as rods in microscale with clear variation in size, dimensionality and loss of sharp edges [Figure 16 d-f](#). EDS analysis [Figure 18](#) for this catalyst confirms the presence of sodium in the final structure with the lowest weight percentage compared to Zinc, oxygen and chloride. [Figure 16 g-i](#) showing the surface morphology for third catalyst ZnLDH-Cl/NH₃. Loss of regular growth is clearly observed by using NH₃ base resulting in the formation of microscale catalyst particles. EDS analysis [Figure 19](#) indicated an appreciable amount of zinc observed in this catalyst, regarded as the highest among all three prepared catalysts with the low weight percentage of nitrogen. Uneven distribution of atoms has also been observed from EDS mapping for this catalyst. Discrepancy in the observed structural morphology behavior for the three prepared catalysts can be attributed to the type and strength of the used base, as it can control how harsh or mild reaction conditions which are reflected directly in particle growth [224].

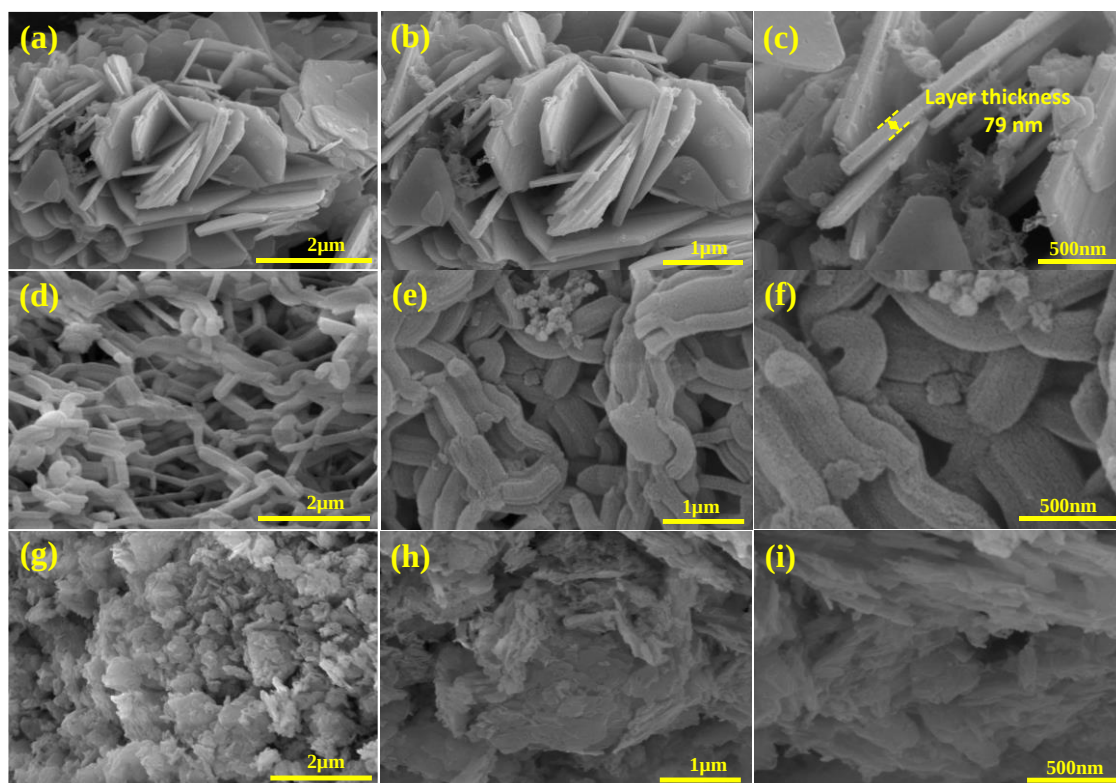


Figure 16: FE-SEM for ZnLDH-Cl/Ca (a-c), ZnLDH-Cl/Na (d-f) and ZnLDH-Cl/NH (g-i) electrocatalysts.

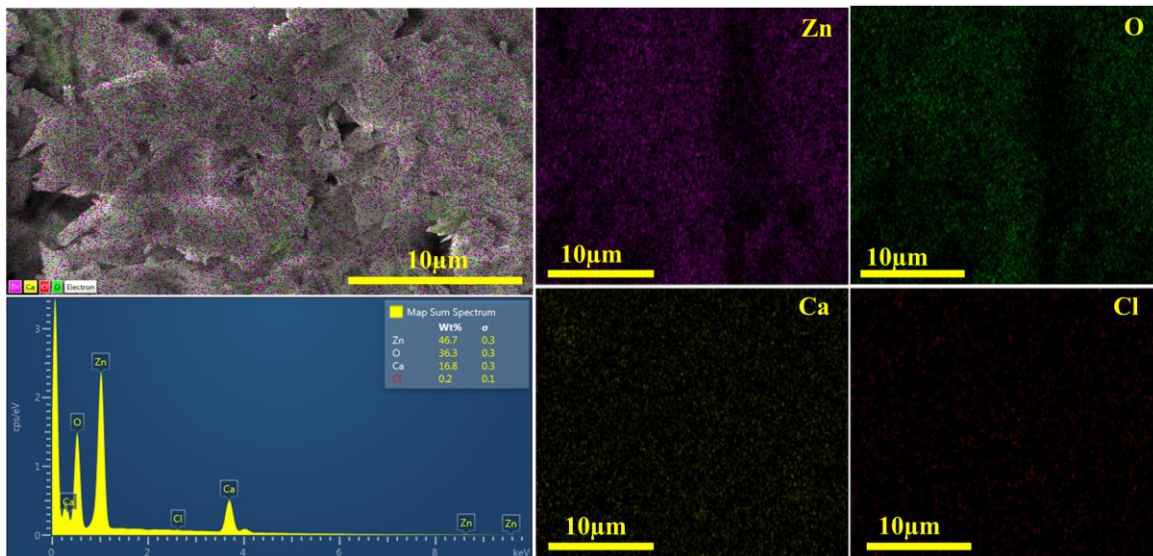


Figure 17: SEM image with EDS mapping of ZnLDH-Cl/Ca catalyst

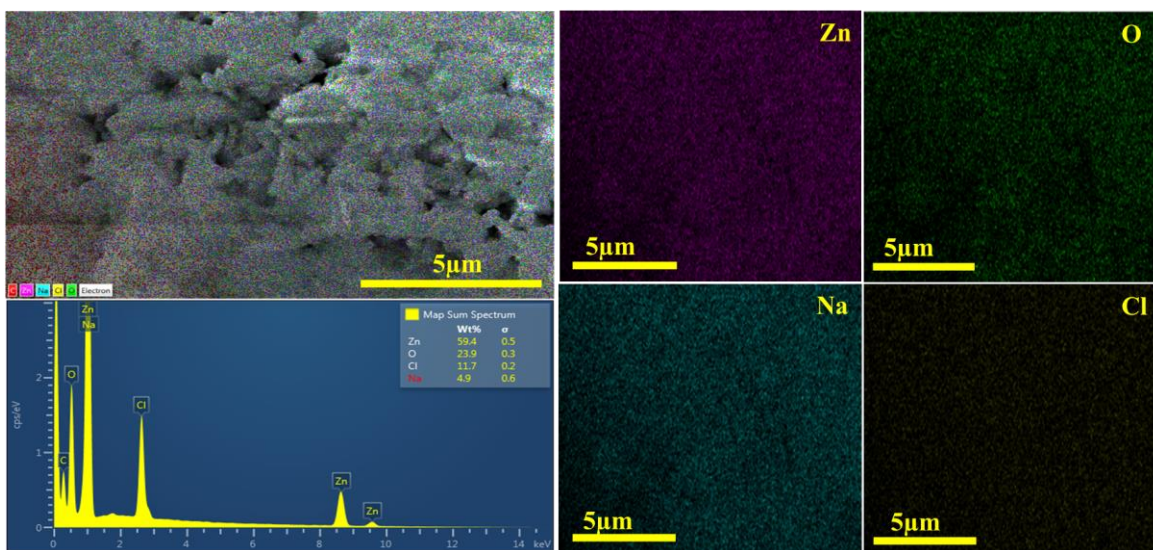


Figure 18: SEM image with EDS mapping of ZnLDH-Cl/Na catalyst

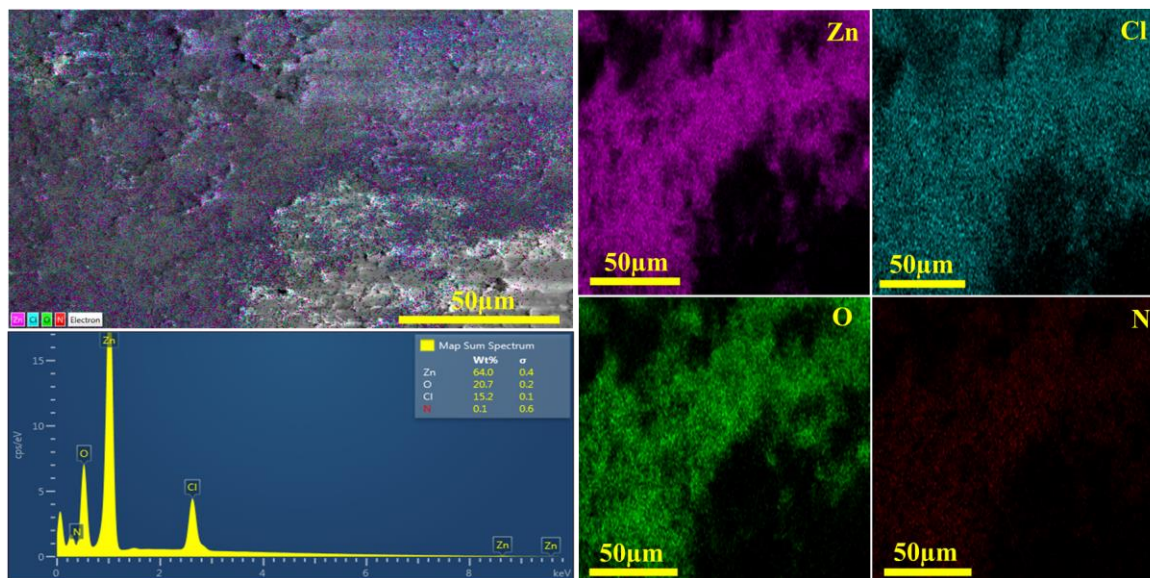


Figure 19: SEM image with EDS mapping of ZnLDH-Cl/NH catalyst

4.4 Transmitted Electron Microscopy TEM Analysis

Micromorphology of the three prepared catalysts has been investigated by employing TEM. The resulting micromorphology from Zn-LDH-Cl/Ca showed a typical trigonal structure with high crystallinity **Figure 20 a-c**. Selected area diffraction SAD showed a crystalline structure and, it can be indexed to trigonal planes 100 and 101 for ZnO lattice with interplanar spacing of 0.282 nm, 0.232 nm, for indexed planes, respectively and 003 phase with interplanar spacing of 0.26 nm assigned for zinc layered double hydroxide. The trigonal layer appeared dark in **Figure 20a**, indicating multilayers stuck on each other. This considers one of the characteristics of LDHs materials, which explains the lattice mismatch in **Figure 20b**. Asymmetrical layered structure observed with ZnLDH-Cl/Na appearing with a bright color indicated of less layer thickness compared with ZnLDH-Cl/Ca and small crystallin particles refer to zinc oxide resulted of annulated the sample at 180 °C **Figure 20d**. This crystalline particle exhibited a higher interplanar

spacing of 0.301 nm and 0.241 nm for 100 and 101 crystallographic planes respectively, as shown in **Figure 20e**. Also, the micrograph for ZnLDH-Cl/NH reflected high Zn concentration zones unevenly distributed over the catalyst **Figure 20g** while SAD showed 0.314 nm and 0.186 nm for ZnO₁₀₀ and ZnO₁₀₂ [225].

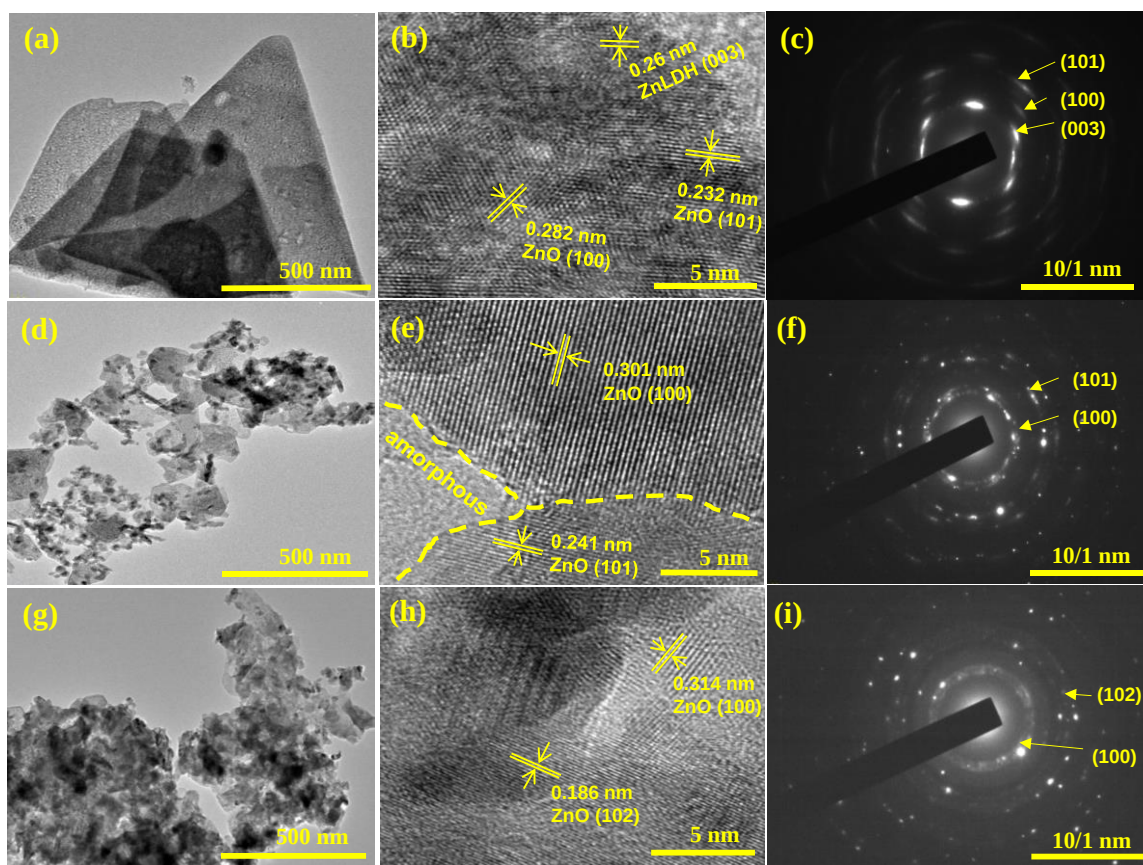


Figure 20: TEM for ZnLDH-Cl/Ca (a-c), ZnLDH-Cl/Na (d-f) and ZnLDH-Cl/NH (g-i) catalyst

4.5 X-ray Photoelectron Spectroscopy XPS Analysis

The surface chemical state of as prepared ZnLDH-Cl/Ca catalyst has been investigated using XPS, as shown in **Figure 21**. a set of two peaks was observed at 1044.09 eV and 1021.10 eV in which were assigned to Zn 2P as Zn 2P_{1/2} and Zn 2P_{3/2}

respectively **Figure 21d**. These ascribed peaks indicate that the valence state for Zn in the prepared catalyst is +2 [226,227]. The weight percent analysis **Table 1** shows that the zinc existed as Zn 2P_{3/2} with weight % of 51.26 which represents the highest value among the other elements. The C 1s spectra were measured as internal standard to correct any shift in peak position, and it showed two deconvoluted peaks positioned at 289.28 eV and 284.8 eV, corresponding to C=O and C-C respectively [226], as indicated in **Figure 21f**. for O 1s as shown in **Figure 21c**, three peaks were observed for three types of oxygen at 531.48, 530.83 and 529.92 eV, and it can be assigned for Zn-OH, -OH and ZnO respectively [228,229]. A unique doublet peak with separation of about 3.5 eV appeared, and it corresponds to Ca 2p with values of 350.33 eV and 346.78 eV ascribed to Ca 2P as Ca 2P_{1/2} and Ca 2P_{3/2} respectively, which can be attributed to Ca in +2 valence state **Figure 21a** [230]. In addition, weight% analysis demonstrated that the Ca existed in Ca 2P_{3/2} form with weight% of 11.32 **Table 1**. Another doublet peak was obtained at 201.63 eV and 200.03 eV for organic chlorine Cl 2P as Cl 2P_{1/2} and Cl 2P_{3/2}, respectively **Figure 21b**. The weight% analysis showed that the chlorine is expected as Cl 2P_{3/2} with weight% of 7.3, and the survey analysis was demonstrated in **Figure 21e**.

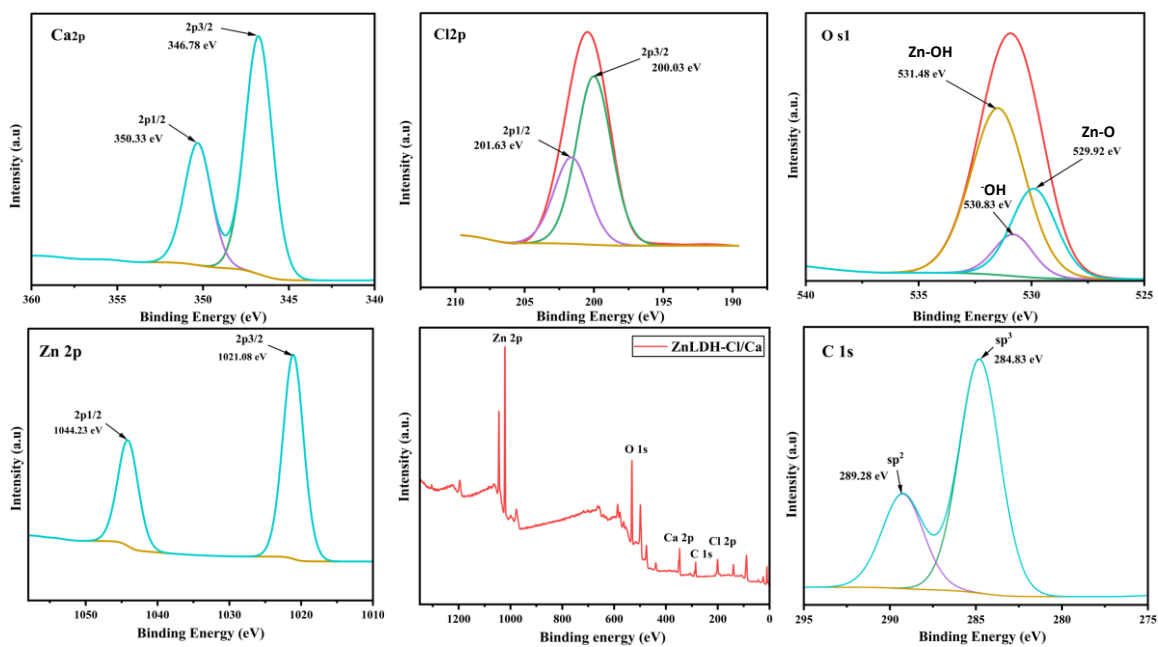


Figure 21: XPS analysis for ZnLDH-Cl/Ca electrocatalyst

Table 1: XPS Analysis Data for ZnLDH-Cl/Ca Electrocatalyst

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Weight %	Q
Ca2p1 A	350.31	1.86	43346.02	0	0
Zn2p1 A	1044.1	1.93	389268.26	0	0
Cl2p1 A	202.11	1.77	20494.9	0	0
C1s B	289.25	2.85	16838.44	2.89	1
C1s A	284.79	2.79	40495.87	6.94	1
Cl2p3 A	200.31	1.87	50494.9	7.3	1
Ca2p3 A	346.76	1.86	84423.94	11.32	1
O1s A	531.48	2.44	147727.65	12.29	1
O1s B	530.83	2.28	87627.65	5.80	1
O1s C	529.92	2.19	57927.65	2.20	1
Zn2p3 A	1021.09	1.93	751526.07	51.26	1

4.6 Electrochemical Assessments

As outlined in the literature, the electrochemical performance of the catalysts under study was carried out in a three-electrode configuration system, commonly called an H-cell system [231,232]. The working electrode in this system consisted of the as-prepared ZnLDH-Cl/X (X = Ca, Na, and NH) electrode. In contrast, the Pt wire and Ag/AgCl electrode (3.0 M KCl, Autolab) served as the counter electrode and reference electrode, respectively. The electrolyte used in this study was a 0.5 M KHCO₃ solution. It is pertinent to note that the catholyte was continuously purged with CO₂ at a rate of 50 mL/min before the electrolysis process to ensure the electrolyte was saturated with CO₂ and to reduce the pH to 7.4. In addition, it continuously purged with CO₂ at a rate of 5 mL/min during the electrolysis process to maintain the CO₂ in the reaction medium.

LSV was conducted to examine the catalytic materials' conductivity and confirm the onset of CO₂ reduction. The results [Figure 22](#) reveal that the ZnLDH-Cl/Ca catalyst demonstrates notably higher current densities of 16.16 mA cm⁻² when tested in a CO₂-saturated electrolyte compared to the ZnLDH-Cl/Na and ZnLDH-Cl/NH catalysts which exhibited 8.5 mA cm⁻² and 7.73 mA cm⁻² respectively revealing the highest CO₂-ECR over ZnLDH-Cl/Ca electrocatalyst. Furthermore, when the same tests were conducted in an Ar-saturated electrolyte, it became evident that the ZnLDH-Cl/Ca electrodes exhibit remarkable activity for CO₂ reduction, exhibiting significantly higher current density than the ZnLDH-Cl/Na and ZnLDH-Cl/NH catalysts. These current densities represent a significant improvement compared to the performance of bulk Zn catalysts, which typically yield current densities of less than 3 mA cm⁻² at -

1.0 V versus RHE [233,234]. This enhanced performance can be attributed to the presence of calcium metal ions within the 2D layer in ZnLDH-Cl/Ca which also contributes to the current density. Due to its electrical conductivity as established in literature [235].

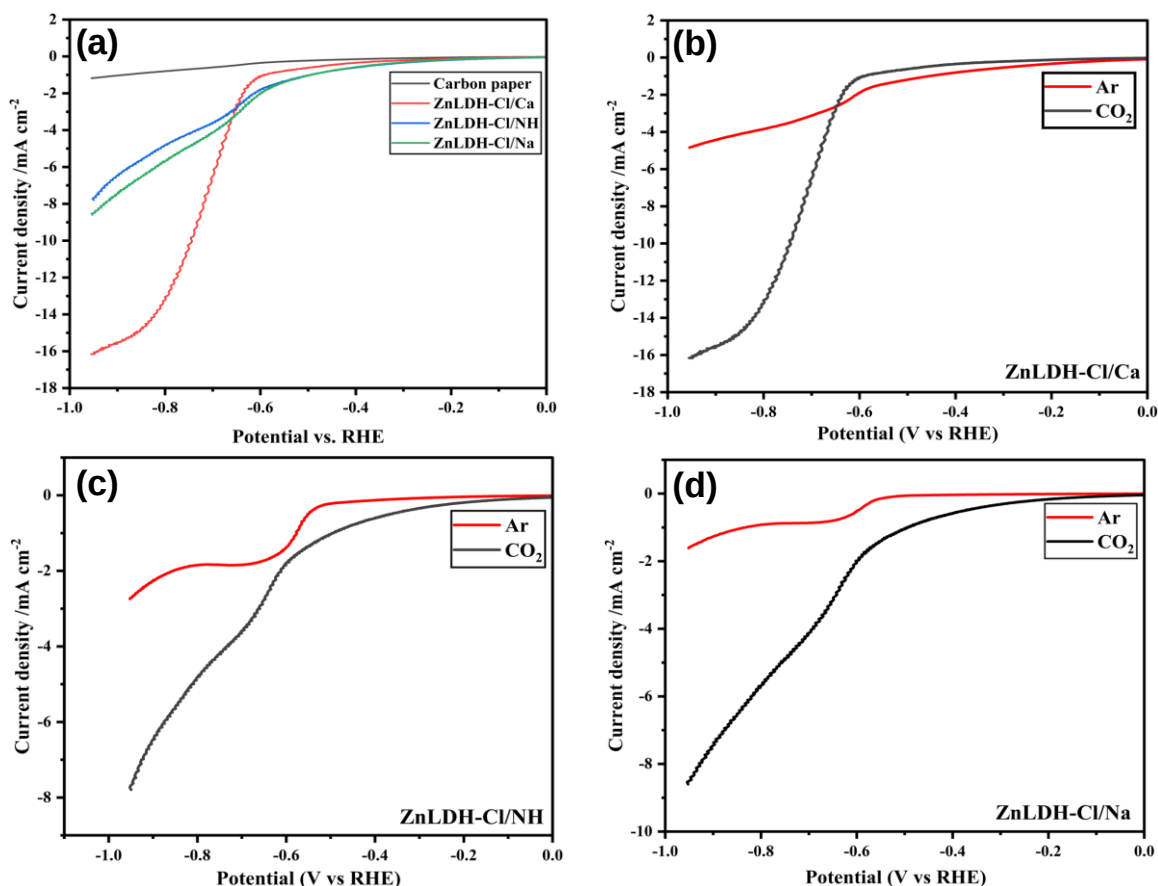


Figure 22: Linear sweep voltammetry scan for as prepared catalyst in (a) CO₂-saturated electrolyte, (b) ZnLDH-Cl/Ca in Ar-saturated electrolyte, (c) ZnLDH-Cl/NH in Ar-saturated electrolyte, (d) ZnLDH-Cl/Na in Ar-saturated electrolyte.

To gain a more comprehensive understanding of the CO₂ reduction reaction (CO₂-ECR) activity and product distribution, potentiostatic CO₂ electrolysis experiments were conducted within the potential range of -1.2 V to -1.6 V versus Ag/AgCl reference electrode, employing the ZnLDH-Cl/Ca, ZnLDH-Cl/Na, and ZnLDH-Cl/NH as working electrodes. The primary outcome resulting from the CO₂ electrolysis employing the ZnLDH-Cl/Ca electrode is carbon monoxide, with the concurrent detection of a small quantity of hydrogen observed at high overpotentials when utilizing ZnLDH-Cl/Na and ZnLDH-Cl/NH electrodes (Figure 23). This observation signifies the incidental generation of hydrogen as a byproduct during the reduction of water. The catalyst synthesized through the calcium hydroxide route demonstrated the highest CO faradaic efficiency (FE_{CO}) of 99.7 at an applied potential of 0.966 V vs RHE. In contrast, the catalyst prepared using sodium hydroxide exhibited a lower FE_{CO} of 75.06 at the same applied potential. Furthermore, the catalyst synthesized via ammonium hydroxide displayed the lowest FE_{CO} of 56.54, as illustrated in Figure 23a. These results underscore the influence of the nature of the hydroxide source and the type of cations incorporated within the layers on the faradaic efficiency of carbon monoxide production. Also, this activity can be attributed to the variation in morphology. As the literature states, morphology significantly influences activity selectivity and faradaic efficiency [6]. In addition, the presence of calcium ions within the layers plays a significant role in maximizing the efficiency and activity of layered double hydroxide materials [236] as exhibited by ZnLDH-Cl/Ca electrocatalyst.

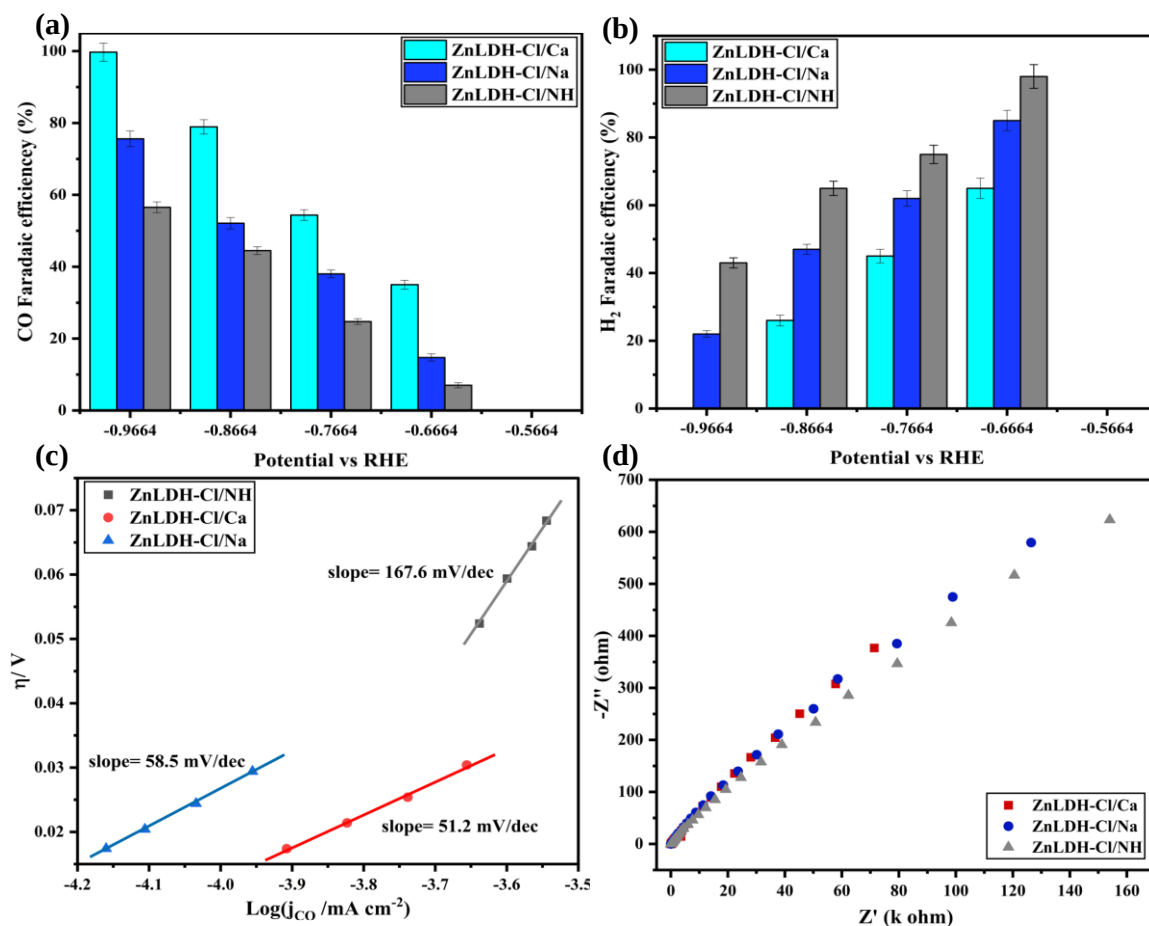


Figure 23: The faradaic efficiency of as prepared catalysts (a) FE of CO product, (b) FE of H₂ product, (c) Tafel plot of as synthesized catalysts, (d) the EIS result of as prepared catalysts.

The ZnLDH-Cl/Ca electrocatalyst displayed a high crystalline nature and a trigonal 2D layered morphology and demonstrated exceptional performance in CO₂ electrochemical reduction, particularly in excellent faradaic efficiency. The well-defined crystalline structure implies a precise arrangement of atoms on the catalyst surface, creating a wealth of active sites conducive to efficient CO₂ adsorption and subsequent conversion. The trigonal 2D layered morphology further enhances the catalyst's electrochemical activity.

This specific structural configuration provides an extended surface area and exposes more active sites, optimizing the catalyst's interaction with CO₂ molecules. The layered structure allows for enhanced mass transport and facilitates the diffusion of reactants to active sites, minimizing undesired side reactions and promoting the desired electrochemical reduction of CO₂. Furthermore, the good synergy between the Ca⁺² and Zn⁺² led to excellent improvement of faradaic efficiency towards CO formation. In addition, the favourable CO desorption on the calcium-based catalyst is confirmed by Wang et al. [237], which reveals that the leading active site responsible for CO₂-ECR is the Ca2p/3 within the catalyst structure. The activity of ZnLDH-Cl/Na can be attributed to the zinc oxide phase within the catalyst structure since the maximum faradaic efficiency within the range of the zinc oxide electrocatalyst [238,239,240], which indicates that the sodium does not play any role in terms of performance. Also, the low performance compared to the ZnLDH-Cl/Ca catalyst can be explained by the lack of active sites resulting from the agglomeration of rods, which leads to the formation of a layer-like structure where the rods align in two dimensions, causing a reduction in surface area and the partial removal of active sites at the edges. ZnLDH-Cl/NH catalysts displayed poor crystalline nature, indistinct morphology, and low faradaic efficiency in CO₂ electrochemical reduction, often facing challenges in facilitating efficient and selective conversion of CO₂ to desired products. The lack of a well-defined crystalline structure can result in a disordered arrangement of atoms on the catalyst surface, leading to fewer active sites and compromised catalytic performance. Additionally, the absence of a distinguished morphology may indicate irregularities in the catalyst surface, hindering optimal CO₂ adsorption and interaction with reactive sites. The poor faradaic efficiency in CO₂ electrochemical reduction suggests that

a significant portion of the electrical current is being diverted towards undesired side reactions HER or inefficient pathways, rather than being utilized for the targeted conversion of CO₂ to valuable products. This inefficiency could be attributed to a lack of well-defined active sites, inadequate charge transfer kinetics, or defects in the catalyst structure.

The electrochemical impedance spectroscopy (EIS) method was utilized to investigate the charge transfer characteristics of the catalysts synthesized in this research. **Figure 23d** presents Nyquist plots of ZnLDH-Cl/Ca, ZnLDH-Cl/Na, and ZnLDH-Cl/NH in 0.5 M KHCO₃ solutions. This study made use of a similar circuit that ran in parallel with a solution resistance (R_1), a phase element (CPE1), and a charge transfer resistance (R_2). Notably, the EIS results revealed that ZnLDH-Cl/NH exhibited a remarkably high charge transfer resistance (R_2) of 154 Ω , limiting its activity towards CO₂-ECR. Conversely, the R_2 values of ZnLDH-Cl/Na were significantly reduced to 126.4 Ω . The introduction of calcium hydroxide as a source of hydroxide to synthesize ZnLDH-Cl/Ca further diminished this value to 71.3 Ω . This reduction implies a lower charge transfer resistance, thereby favouring the CO₂-ECR process on ZnLDH-Cl/Ca due to the favourable desorption of CO on Ca²⁺ sites within the structure of the ZnLDH-Cl/Ca electrocatalyst. **Figure 23c**, Illustrates Tafel plots depicting overpotential against the logarithm of partial current density for CO [241]. Notably, linear plots within a notably low overpotential range characterize the electrocatalytic behaviour of the ZnLDH-Cl/Ca catalyst. The observed slope of 51.2 mV/dec aligns with a mechanism indicative of a rate-determining initial electron transfer to CO₂, forming of a surface-adsorbed CO₂^{*-} intermediate. This mechanism is commonly associated with metal electrocatalysts [242], highlighting the

significance of the chosen electrocatalyst in facilitating this specific reaction. Similarly, the ZnLDH-Cl/Na electrocatalyst demonstrates linear Tafel plots at a low overpotential range, with a 58.5 mV/dec slope. This behaviour suggests a comparable rate-determining step involving the initial electron transfer to CO₂, consistent with the mechanisms observed in metal electrocatalysts. In contrast, the ZnLDH-Cl/NH electrocatalyst exhibits steep slopes of 167.6 mV/dec at higher overpotential ranges. This observation implies that the electrocatalytic activity of ZnLDH-Cl/NH may be influenced by the combined effects of gas diffusion and ionic mass transport [243]. The substantial change in slope at high overpotentials suggests a shift in the rate-determining step, potentially indicative of altered mechanisms controlling the electrochemical processes. **Figure 24b** provided insights into the stability assessment of the prepared catalyst at 0.966 V vs RHE over 24 hours. The results indicated that the ZnLDH-Cl/Ca electrocatalyst exhibited notable stability, maintaining its performance for up to 24 hours at a consistent current density of approximately 15.80 mA cm⁻². During stability tests, a discernible increase in current density was observed for the ZnLDH-Cl/Na electrocatalyst, reaching up to about 8.0 mA cm⁻². This observation suggests that the selected catalyst not only preserves its electrocatalytic activity but may also undergo beneficial modifications over prolonged electrochemical operation. However, the ZnLDH-Cl/NH electrocatalyst demonstrated stability up to 20.8 hours with a current density of 8.5 mA cm⁻², accompanied by a degradation in its performance. This decline may be attributed to surface passivation, undesired side reactions, or limitations in the active sites responsible for the CO₂-ECR. For ZnLDH-Cl/Ca electrocatalyst, the faradaic efficiency was evaluated throughout the stability test **Figure 24b**, and the finding showed that the electrocatalyst demonstrated high

performance and maintained an excellent production rate for CO for up to 24 hours with an approximately constant current density of around 15.8 mA cm^{-2} .

The investigation of the electrochemical active surface area (ECSA) of the electrodes was conducted through the application of the double-layer capacitance (Cdl) method [244]. CV were systematically recorded in non-Faradaic regions at varying scan rates (10, 20, 40, 60, 80, and 100 mV sec^{-1}) using CO_2 -saturated 0.5 M KHCO_3 as the electrolyte solution. The obtained data revealed a direct proportionality between the number of scans and voltammograms, indicative of a corresponding relationship between Cdl and ECSA, as illustrated in **Figure 24c** for the ZnLDH-Cl/Ca electrode.

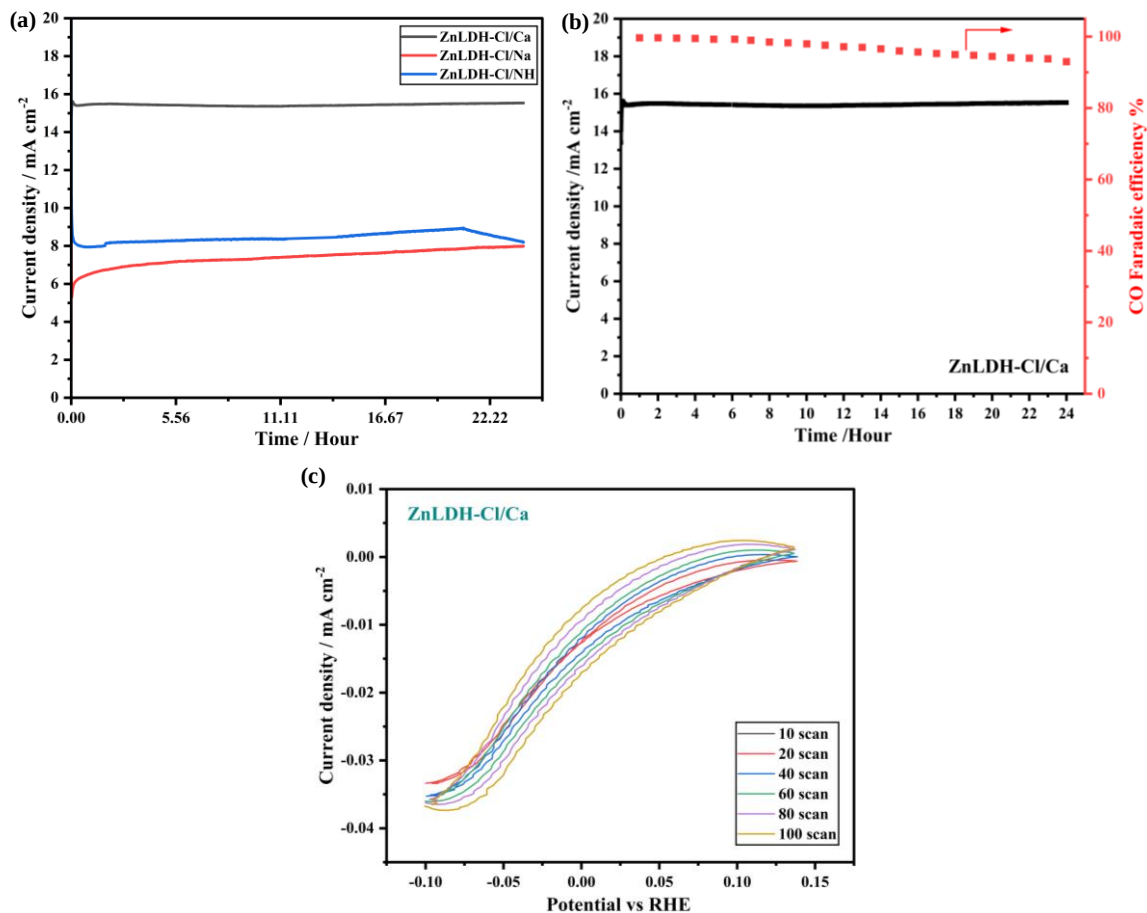


Figure 24: (a) Stability test of as-prepared catalysts, (b) Faradaic efficiency of ZnLDH-Cl/Ca with current density throughout the stability test, (c) Cyclic voltammetry scan for the ZnLDH-Cl/Ca electrocatalyst.

4.7 Conclusion

The ZnLDH-Cl catalysts were successfully synthesized through hydrolysis procedures conducted under specific conditions, employing a CO₂-saturated KHCO₃ electrolyte. This synthetic approach was undertaken to assess the electrocatalytic efficacy of ZnLDH-Cl electrocatalysts in the electrochemical reduction of CO₂. The synthesis involved the utilization of three distinct sources of hydroxide, namely, Ca(OH)₂, NaOH, and NH₄OH, to produce zinc-layered double hydroxide-based catalysts denoted as ZnLDH-Cl/Ca, ZnLDH-Cl/Na, and ZnLDH-Cl/NH, respectively. Various characterization techniques were employed to analyze the synthesized catalysts comprehensively. XRD methods facilitated the determination of crystal structures, while microscopic imaging techniques, including SEM and TEM, provided insights into the morphological features. EDS offered elemental composition data, while XPS for surface analysis and Fourier-FTIR were employed for the identification of the functional group. Additionally, chromatographic techniques, encompassing gas chromatography and liquid chromatography, were integrated with diverse detectors such as flame ionization detector (FID), thermal conductivity detector (TCD) to qualitative and quantitative determination of the final products. Among the catalysts investigated ZnLDH-Cl/Ca demonstrated exceptional efficacy and high selectivity in CO formation. At an applied potential of 0.966 V vs. RHE, ZnLDH-Cl/Ca exhibited a remarkable faradaic efficiency (FE) of 99.7% and a total current density of 5 mA cm⁻². In contrast, ZnLDH-Cl/Na and ZnLDH-Cl/NH catalysts displayed FE_{CO} of 75.6 and 56.54, respectively, under identical experimental conditions. Furthermore, regarding stability, the ZnLDH-Cl/Ca catalyst sustained high stability for up to 24 hours, maintaining an approximately constant current density throughout the

assessment. This study underscores the promising electrocatalytic performance and stability of ZnLDH-Cl/Ca in the context of CO₂ reduction. In addition, this research could open the way for the long-term development of CO₂ conversion electrocatalysts that can be both effective and potentially cost-effective on an industrial scale.

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PUBLICATIONS

S/N	Journal	IF	Q-Rank
1	Omar Ahmed Taialla, Mustapha Umar, AbdulHakam Shafiu Abdullahi, Esraa Kotob, Mohammed Mosaad Awad, Aliyu Musa Alhassan, Ijaz Hussain, Saheed A. Ganiyu and Khalid Alhooshani “Unlocking the potential of ZIF-based electrocatalysts for electrochemical reduction of CO ₂ : Recent advances, current trends, and Machine Learnings”. Under review in the Coordination Chemistry Reviews	20.6	Q1
2	Taialla OA , Umar Mustapha, Khalid Omer, AbdulHakam Shafiu Abdullahi, Mohammed Mosaad Awada, Saheed A. Ganiyu and Khalid Alhooshani “Morphology- Controlled Synthesis of Zinc Layered Double Hydroxide for Electrocatalytic CO ₂ Reduction” (under process for publication).		

3	Abdullahi Abdulhakam, Mustapha Umar, Ijaz Hussain, Omer A. Taialla , Esraa Abas, Mohammed Ali, Basiru O. Yusuf, Ismail Abdulazeez, Saheed A. Ganiyu, Khalid R. Alhooshani "Review of recent advancements in the electrocatalytic reduction of CO ₂ to Formate/Formic acid: the role of conducting polymers". Submitted to Coordination Chemistry Reviews	20.6	Q1
4	Awad MM, Hussain I, Taialla OA , Ganiyu SA, Alhooshani K, "Syngas Production using Fibrous Silica Zinc Oxide (FSZ) Supported Nickel Catalyst: An Innovative catalytic system for Dry Reforming of Methane" (in Preparation).		
5	Awad MM, Hussain I, Taialla OA , Ganiyu SA, Alhooshani K, "Superior Performance of Unique Fibrous Structured Silica Lanthanum Oxide-Supported Nickel Catalyst (Ni/FSL) for Dry Reforming of Methane (DRM)" Journal of Cleaner Production, 2023 (Submitted) .	11.9	Q1
6	Awad MM, Hussain I, Mustapha U, Taialla OA , Alhassan A, Abdullahi AS, Ganiyu SA, Alhooshani K, "A critique of synergistic effects between catalytic and physiochemical properties for dry reforming of methane: emerging trends, current challenges, and machine learning", 2023 Submitted to energy conversion and management .	11.5	Q1
7	Alhassan AM, Hussain I, Taialla OA , Awad MM, Tanimu A, Alhooshani K, Ganiyu SA, "Advances in catalytic dry reforming of methane (DRM): Emerging trends, current challenges, and future perspectives" Journal of Cleaner Production, 2023, 138638 .	11.9	Q1
8	Basiru O Yusuf, Mustapha Umar, Esraa Kotob, Abdullahi Abdulhakam, Taialla OA , Mohammed Mosaad Awad, Ijaz Hussain, Khalid R Alhooshani, Saheed A Ganiyu "Recent Advances in Bimetallic Catalysts for Methane Steam Reforming in Hydrogen Production: Current Trends, Challenges, and Future Prospects" Chemistry – An Asian Journal, 2023	4.1	Q1

Conferences paper/poster presentation

Taialla OA, Umar Mustapha, Khalid Omer, AbdulHakam Shafiu Abdullahi, Mohammed Mosaad Awada, Saheed A. Ganiyu and Khalid Alhooshani "Morphology- Controlled Synthesis of Zinc Layered Double Hydroxide for Electrocatalytic CO₂ Reduction" **32ed Saudi Japan Symposium,2023 (Accepted)**