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Fabrication of High-Performance Electrocatalytic Electrode for Hydrogen Evolution reaction HER

Presented by: MANSOURIA Chaima

Examination Committee

Pr. D. SELLOUM	University Setif 1	Chairperson
Dr. Y. MESSAOUDI	University Setif 1	Supervisor
Pr. S. LEGHRIB	University Setif 1	Examiner

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GENERAL INTRODUCTION

The increasing global demand for energy, coupled with growing environmental concerns and the progressive depletion of fossil fuel resources, has intensified the search for sustainable and low-carbon energy technologies. Despite their dominant contribution to the global energy supply, fossil fuels remain one of the primary sources of greenhouse gas emissions, which significantly contribute to climate change and environmental degradation. Consequently, the transition toward renewable and environmentally friendly energy systems has become a major global priority [1,2].

Among the various alternative energy carriers, hydrogen has emerged as one of the most promising candidates for future energy systems owing to its high energy density, environmental compatibility, and versatility in energy conversion and storage applications. When utilized in fuel cells, hydrogen produces only water as a by-product, making it an attractive solution for reducing carbon emissions and supporting the transition toward a sustainable energy economy [3,4].

The sustainability of hydrogen technologies, however, strongly depends on the method used for hydrogen production. Among the available production routes, electrochemical water splitting has attracted considerable attention because it enables the generation of high-purity hydrogen using electricity derived from renewable sources such as solar and wind energy. This technology is considered a key pathway toward green hydrogen production and large-scale energy storage in future renewable energy infrastructures [5,6].

Water electrolysis involves two electrochemical half-reactions: the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. Although electrolysis is environmentally benign, its widespread implementation remains limited by kinetic losses and energy efficiency challenges. Therefore, the development of efficient electrocatalysts capable of accelerating the HER while reducing energy consumption is essential for improving the overall performance of water-splitting systems [7,8].

Platinum-based materials are currently regarded as benchmark HER electrocatalysts because of their exceptional catalytic activity and favorable hydrogen adsorption characteristics. However, their high cost, scarcity, and limited long-term economic viability restrict their practical application in large-scale hydrogen production. As a result, extensive research efforts have been directed toward the development of low-cost and earth-abundant alternatives based on transition-metal compounds [9].

Among the various non-noble-metal catalysts investigated, transition-metal sulfides have emerged as particularly attractive candidates owing to their favorable electronic structure, high electrical conductivity, chemical stability, and abundant active sites. Furthermore, the construction of heterostructured sulfide systems has been shown to enhance catalytic performance through synergistic interactions, accelerated charge transfer, and improved utilization of active sites [10,11].

In this context, the present work focuses on the synthesis and evaluation of CuS, CoS, and CuS/CoSbased electrocatalytic electrodes supported on nickel foam for alkaline hydrogen evolution. The prepared electrodes were fabricated by electrodeposition followed by sulfurization treatment and characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray fluorescence spectroscopy (XRF). Their electrocatalytic performance toward HER was systematically investigated using linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), electrochemical double-layer capacitance (C_{dl}), electrochemically active surface area ($ECSA$), turnover frequency (TOF), and stability measurements. The main objective of this study is to establish the relationship between the structural and electrochemical properties of the prepared electrodes and their hydrogen evolution performance, while identifying an efficient and cost-effective electrocatalyst for alkaline water electrolysis.

This manuscript is organized into three chapters. Following a general introduction highlighting the importance of hydrogen as a clean energy carrier and the role of electrocatalysts in sustainable hydrogen production, the first chapter presents a literature review on water electrolysis, the hydrogen evolution reaction (HER), and the development of transition-metal sulfide electrocatalysts, with particular emphasis on $CuS, CoS,$ and heterostructure-based materials.

The second chapter describes the materials, experimental procedures, and characterization techniques employed in this work. It includes the synthesis of CuS, CoS, and CuS/CoS electrodes on nickel foam by electrodeposition followed by sulfurization, as well as the physical and electrochemical methods used for their characterization.

The third chapter presents and discusses the experimental results obtained from structural, morphological, compositional, and electrochemical analyses. Particular attention is devoted to

evaluating the HER performance of the prepared electrodes through XRD, SEM, XRF, LSV, Tafel analysis, $EIS, ECSA, TOF$, and stability measurements. Finally, the thesis concludes with a general conclusion summarizing the main findings and perspectives of this study.

Abstract

Hydrogen is a promising clean energy carrier for sustainable energy applications. In this work, CuS, CoS, and CuS/CoS electrocatalysts were synthesized on nickel foam by electrodeposition followed by sulfurization and evaluated for the hydrogen evolution reaction (*HER*) in alkaline medium. Structural and morphological characterization was performed using *XRD, SEM, and XRF,* while electrochemical performance was investigated by *LSV, CV, EIS, ECSA, TOF*, and stability measurements. The results demonstrated that the $NF/CuS/CoS$ electrode exhibited the highest *HER* activity, attributed to its improved charge-transfer properties, larger active surface area, and synergistic heterostructure effect. These findings highlight the potential of CuS/CoS heterostructures as efficient and cost-effective electrocatalysts for alkaline hydrogen production.

Résumé

L'hydrogène est un vecteur énergétique propre prometteur pour les applications énergétiques durables. Dans ce travail, des électro catalyseurs à base de CuS, CoS et CuS/CoS ont été synthétisés sur mousse de nickel par électrodéposition suivie d'un traitement de sulfurisation, puis évalués pour la réaction d'évolution de l'hydrogène (*HER*) en milieu alcalin. La caractérisation structurale et morphologique a été réalisée par diffraction des rayons X (*DRX*), microscopie électronique à balayage (*MEB*) et fluorescence X (*XRF*), tandis que les performances électrochimiques ont été étudiées par voltampèremètre à balayage linéaire (*LSV)*, voltampèremètre cyclique *(CV),* spectroscopie d'impédance électrochimique (*EIS*), détermination de la surface électro chimiquement active (ECSA), fréquence de renouvellement catalytique (*TOF*) et tests de stabilité. Les résultats ont montré que l'électrode $NF/CuS/CoS$ présente la meilleure activité *HER*, grâce à ses propriétés améliorées de transfert de charge, à sa surface active plus développée et à l'effet synergique de l'hétérostructure. Ces résultats mettent en évidence le potentiel des hétérostructures CuS/CoS comme électrocatalyseurs efficaces et économiques pour la production d'hydrogène en milieu alcalin.

الملخص

يُعدّ الهيدروجين ناقلًا واعدًا للطاقة النظيفة للتطبيقات الطاقوية المستدامة. في هذا العمل، تم تحضير محفزات كهربائية من CuS وCoS وCuS/CoS على ركيزة من رغوة النيكل بواسطة الترسيب الكهروكيميائي متبوعًا بمعالجة الكبريتة، ثم تقييم أدائها في تفاعل تطور الهيدروجين (HER) في وسط قلوي. تم توصيف البنية والتركيب المورفولوجي باستخدام حيود الأشعة السينية(XRD) ، والمجهر الإلكتروني الماسح(SEM) ، وفلورة الأشعة السينية(XRF) ، بينما تم تقييم الأداء الكهروكيميائي بواسطة الفولتمترية الخطية(LSV) ، والفولتمترية الدورية(CV) ، ومطيافية الممانعة الكهروكيميائية(EIS) ، وحساب المساحة السطحية النشطة كهربائيًا(ECSA) ، وتردد الدوران التحفيزي (TOF)، واختبارات الاستقرار. أظهرت النتائج أن القطب NF/CuS/CoS يمتلك أفضل نشاط تجاه تفاعل تطور الهيدروجين، ويُعزى ذلك إلى تحسن خصائص انتقال الشحنة، وارتفاع عدد المواقع النشطة، والتأثير التآزري للبنية غير المتجانسة. وتبرز هذه النتائج إمكانات هياكل CuS/CoS غير المتجانسة كمحفزات كهربائية فعالة ومنخفضة التكلفة لإنتاج الهيدروجين في الوسط القلوي