

Energy transition and hydrogen evolution

Energetska tranzicija i vodonična evolucija

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Abstract: The escalating concerns over climate changes and environmental disturbances resulting from anthropogenic influence have propelled the scientific community to seek efficient models for the energy transition. Hydrogen emerges as a promising energy carrier with the potential to replace fossil fuels and mitigate global warming, a pressing threat to life on Earth. This research paper primarily focuses on the electrolytic production of hydrogen, deemed the environmentally acceptable method for this purpose. The central emphasis lies in enhancing the electrodes utilized in this process to elevate the significance of the Hydrogen Evolution Reaction (HER). By improving HER, a pivotal step in the hydrogen production process, the trajectory of civilization's evolution can be positively influenced.

Keywords: green economy, hydrogen, innovation, alkaline electrolysis, energy transition.

Sažetak: Sve veća zabrinutost zbog klimatskih promena i ekoloških poremećaja koji su rezultat antropogenog uticaja naterali su naučnu zajednicu da traži efikasne modele za energetska tranziciju. Vodonik se pojavljuje kao perspektivan nosilac energije sa potencijalom da zameni fosilna goriva i ublaži globalno zagrevanje, goruću pretnju životu na Zemlji. Ovaj istraživački rad se prvenstveno fokusira na elektrolitičku proizvodnju vodonika, koja se smatra ekološki prihvatljivom metodom za ovu svrhu. Centralni naglasak je na poboljšanju elektroda koje se koriste u ovom procesu kako bi se podigao značaj reakcije evolucije vodonika (HER). Poboljšanjem HER, ključnog koraka u procesu proizvodnje vodonika, može se pozitivno uticati na putanju evolucije civilizacije.

Ključne reči: zelena ekonomija, vodonik, inovacije, alkalna elektroliza, energetska tranzicija.

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INTRODUCTION

Escalating global consumption of raw materials, goods, and energy, catalyzed by unprecedented population growth, has engendered deleterious repercussions on the environment and human health (Ehrlich & Holdren, 1971). A pronounced disparity between population growth and the consumption of natural resources is precipitating pervasive environmental challenges on a global scale. Heightened energy demands necessitate the conceptualization and integration of novel energy sources as potential replacements for fossil fuels.

Anthropogenic greenhouse gases (GHG) emissions, specifically carbon dioxide (CO₂), and a prevailing dependency on fossil fuel energy, underscore the pressing need to transition to alternative energy sources (Pacala & Socolow, 2004). This, in turn, incentivizes the industrial sector to invest in transformative technologies. The primary challenge humanity currently faces is curtailing CO₂ emissions to preempt a global temperature escalation exceeding 2°C relative to pre-industrial levels (Stocker et al., 2013).

The anthropogenic deterioration of the environment necessitates urgent action and investment aimed at sustaining planetary and terrestrial life (Steffen et al., 2015). The notion of 'investment' encapsulates not only fiscal contributions but also psychological investments targeting shifts in human habits and attitudes. It is only upon achieving these changes can material investments yield favorable outcomes from both an ecological and economic perspective. Consequent to the magnitude and complexity of the environmental challenges, international governmental cooperation is vital in establishing protective regulations for biodiversity and promoting judicious usage of natural energy sources to facilitate sustainable development (Rockström et al., 2009).

The shift towards renewable energy sources (RES) as an alternative to fossil fuels is being pursued with the objective of addressing these issues (Arsić & Vučinić, 2022; Cvetković et al., 2022). However, the transition to RES utilization necessitates bridging the intermittency in RES-supplied

energy. Hydrogen and hydrogen energy have emerged as potential solutions for this exigency in recent years (Schlapbach & Züttel, 2001). Hydrogen is deemed an indispensable conduit for energy storage and manipulation. Its production can be achieved through various methods, amongst which electrolysis is regarded as the most environmentally compatible (Bockris, 2013). The procurement of hydrogen should ideally meet the criteria of efficiency, environmental suitability, cost-effectiveness, and rapidity. Presently, the most successful method aligning with these prerequisites is alkaline electrolysis integrated with RES. Current research endeavours predominantly focus on enhancing the efficiency of electrolysis, which necessitates the creation of novel electrode materials and innovative production methods (Carmo et al., 2013). The ultimate objective of these efforts is to elevate electrolysis to a critical role in the energy transition and as a medium of planetary decarbonization.

The electrochemical deposition of alloys is subjected to extensive scrutiny due to their promising potential in hydrogen production reactions. Certain literature identifies CoW alloys as prime candidates for this application (Marceta Kaninski et al., 2003). This research paper primarily investigates this facet of the proposed alloy application.

1. MATERIALS AND METHODS

The fabrication of novel electrode coatings entailed parallel experimentation using two distinct deposition bath types: citrate and tartrate. The electroactive constituents for both baths were CoSO₄•7H₂O (Merck®) and Na₂WO₄•2H₂O (Merck®), except for pure Co coatings, where sodium tungstate was omitted. The citrate bath utilized Na₃C₆H₅O₇•2H₂O (trisodium citrate dihydrate, Merck®) as a complexing agent, supplemented with H₃BO₃, and the pH was regulated via the addition of sulfuric acid. The tartrate bath involved the use of Na₂C₄H₄O₆•2H₂O (disodium tartrate dihydrate, Merck®) as a complexing agent, NH₄Cl, and pH adjustment by ammonia addition.

Table 1. Electrochemical baths for deposition of Co-W alloys

Citrate electrodeposition bath					
No.	c(CoSO ₄ •6H ₂ O) / mol dm ⁻³	c(Na ₂ WO ₄ •2H ₂ O) / mol dm ⁻³	c(Na ₃ Cit) / mol dm ⁻³	c(H ₃ BO ₃) / mol dm ⁻³	pH
1.	0.05	0.1	0.15	0.4	6.5
2.	0.05	without	0.15	0.4	6.5
Tartrate electrodeposition bath					
	c(CoSO ₄ •6H ₂ O) / mol dm ⁻³	c(Na ₂ WO ₄ •2H ₂ O) / mol dm ⁻³	c(Na ₂ Tar) / mol dm ⁻³	c(NH ₄ Cl) / mol dm ⁻³	pH
3.	0.05	0.1	1.0	1.0	8.5
4.	0.05	without	1.0	1.0	8.5

In each bath, deposition was performed at a current density (j_t) of: -25, -50, and -100 mA cm⁻² for 1, 0.5 and 0.5 h, respectively. The goal was to maintain consistent charge flow through the cell across all depositions, save for the final case ($j_t = -100$ mA cm⁻²), where the Faraday current was considerably lower than previous instances. Deposition current constancy was ensured using a G750 potentiostat / galvanostat (Gamry Instruments Inc.). All depositions were executed sans additional electrolyte mixing, at ambient temperature. Preceding each deposition, the Ni electrode was cleansed with diethyl ether to eliminate potential organic contaminants, then immersed in a 2:1 nitric acid aqueous solution for two minutes to eradicate inorganic impurities and oxides. Post-immersion, the electrode was thoroughly rinsed with distilled water and transferred to the electrochemical cell (Klueh et al., 2000).

Six distinct Co and W based coatings, and six Co-based coatings, were synthesized and subsequently assessed as catalysts for the Hydrogen Evolution Reaction (HER) in a 6M KOH three-electrode electrochemical cell via chronopotentiometric and polarization curve (Tafel analysis) recordings (Mentus, 2008). The fabricated electrodes served as the working electrodes, a Pt grid functioned as the counter electrode, and a custom-made Hg/HgO electrode in 6M KOH served as the reference electrode. Prior to experimentation, the electrolyte was saturated with hydrogen for 30 minutes. All tested coatings initially underwent hydrogen extraction at a constant current density of $j = -300$ mA cm⁻² for 1200 s, followed by a constant potential value applied for 800 s, yielding a current density more negative than -300 mA cm⁻² for hydrogen extraction. Polarization curves were then recorded, commencing from the applied potential in the second step, changing at a

rate of 1 mV s⁻¹ to a value of approximately -0.90 V, with correction for voltage drop through the electrolyte via the "current interrupt" technique.

The morphologies of the resultant Co-W coatings were scrutinized using Scanning Electron Microscopy (SEM). SEM imagery was captured using a Tescan VEGA TS 5130MM instrument operating at an electron beam energy of 20 keV (Goldstein et al., 2003).

2. RESULTS AND DISCUSSION

The Co and W-based coatings, electrochemically deposited on a nickel substrate from citrate and tartrate baths (Table 1), were assessed as potential catalysts for the Hydrogen Evolution Reaction for implementation in alkaline electrolyzers. The electrocatalytic activities of the electrodes were discerned by comparing the polarization curves (Figure 1) and the electrode potential values relative to a selected reference electrode at a hydrogen extraction current density of -300 mA cm⁻² (E_{300}). The gathered polarization curves insinuate that all the tested coatings displayed superior catalytic activity relative to the pure nickel electrode. The most catalytically active electrode, denoted as CoW1:2tar100, was procured through deposition from a tartrate bath (solution No. 3 in Table 1) at a deposition current density of -100 mA cm⁻². The nomenclature of the tested electrodes is presented in Table 2. Figure 1 illustrates a comparison of the polarization curves of the most and least active Co and W-based electrodes with a pure cobalt electrode and a pure nickel electrode. The E_{300} value, measured relative to the Hg/HgO reference electrode, was employed to compare the catalytic activities of the synthesized coatings. The attained values are delineated in Table 2.

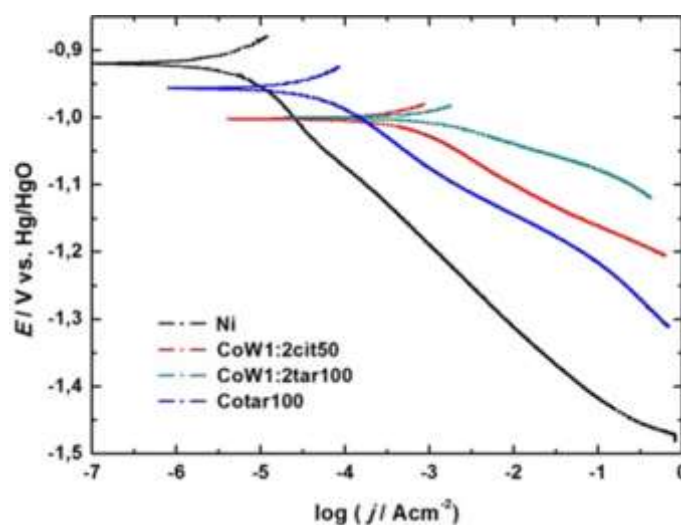


Figure 1. Comparison of polarization curves of the most active and least active CoW electrode with Co and Ni electrodes.

Table 2. E_{300} values and Tafel slopes for electrodes obtained at different parameters of electrochemical deposition

Electrode mark	c(Co):c(W)	Deposition bath	$-j_t / \text{mA cm}^{-2}$	E_{300} / V	$b / \text{mV dec}^{-1}$
Cocit25	1:0	citrate	25	-1,420	61
Cocit50	1:0	citrate	50	-1.373	54
Cocit100	1:0	citrate	100	-1.270	60
Cotar25	1:0	tartrate	25	-1.319	84
Cotar50	1:0	tartrate	50	-1.272	71
Cotar100	1:0	tartrate	100	-1.268	74
CoW1:2cit25	1:2	citrate	25	-1.165	56
CoW1:2cit50	1:2	citrate	50	-1.214	58
CoW1:2cit100	1:2	citrate	100	-1.177	60
CoW1:2tar25	1:2	tartrate	25	-1.145	44
CoW1:2tar50	1:2	tartrate	50	-1.157	46
CoW1:2tar100	1:2	tartrate	100	-1.107	37
Ni	/	/	/	-1.452	120

Electrodes composed of pure cobalt, obtained via electrochemical deposition from a tartrate bath, exhibited comparable activities irrespective of the applied deposition current density. The E_{300} values for these electrodes deviated by a maximum of 50 mV. In contrast, for the Co electrodes derived from the citrate bath, this discrepancy was more pronounced, with the electrode activity enhancing alongside an increase in the deposition current density. At a deposition current density of -100 mA cm^{-2} , it almost matched the activity of the electrodes derived from the tartrate bath.

Based on the polarization curves and E_{300} values, it is deducible that CoW electrodes exhibiting higher activity for the hydrogen evolution reaction are procured through electrochemical co-deposition from a tartrate bath, irrespective of the applied deposition current density. In this instance too, the electrode activities remain notably similar, mirroring the pure Co electrodes obtained from this type of bath.

For pure Co electrodes, Tafel slope values range from 71 to 93 mV dec^{-1} , indicating a decrease with an increase in the deposition current density of the tested coatings. With the significantly more active CoW electrodes, the Tafel slope is lower, spanning from 40 to 60 mV dec^{-1} , which suggests a shift in the reaction mechanism. For the most active electrodes, derived via co-deposition of Co and W from the tartrate bath, the Tafel slope approximates 40 mV dec^{-1} , implying that the limiting step of the hydrogen release reaction is the electrochemical desorption of the adsorbed intermediate, i.e., the Heyrovsky reaction, and the overall mechanism is the Volmer-Heyrovsky mechanism (Mentus, 2008).

The observed alterations in activity and Tafel slopes for the hydrogen evolution reaction of pure cobalt-based electrodes can be predominantly attributed to the surface effect. A surge in deposition current density evidently results in an expansion of the active surface of the resulting electrodes. In the case of CoW electrodes, a notable enhancement in catalytic activity, a reduction in the Tafel slope, and a shift in the reaction mechanism compared to pure Co electrodes are observed, thus indicating a true catalytic effect, in addition to the surface effect.

The morphologies of the electrochemically deposited CoW alloys were scrutinized using Scanning Electron Microscopy, with the resultant images depicted in Figure 2. All CoW coatings exhibit a nodular structure, a characteristic feature of this type of alloy (Su & Huang, 2017). The grain size and shape are significantly influenced by the electrochemical deposition parameters, primarily the composition of the deposition bath and the current density. The grain size variations in CoW alloys with increased deposition current density display different trends contingent on the bath type. With co-deposition from citrate baths, the grain size reduces with current density elevation, whereas the inverse trend is observed with tartrate baths, resulting in the formation of larger grains at a current density of -100 mA cm^{-2} . The morphology of all samples is characterized by the presence of microcracks, detectable along the grain boundaries. These cracks could originate from the vigorous hydrogen evolution during deposition or the strain between the substrate material and the deposited material.

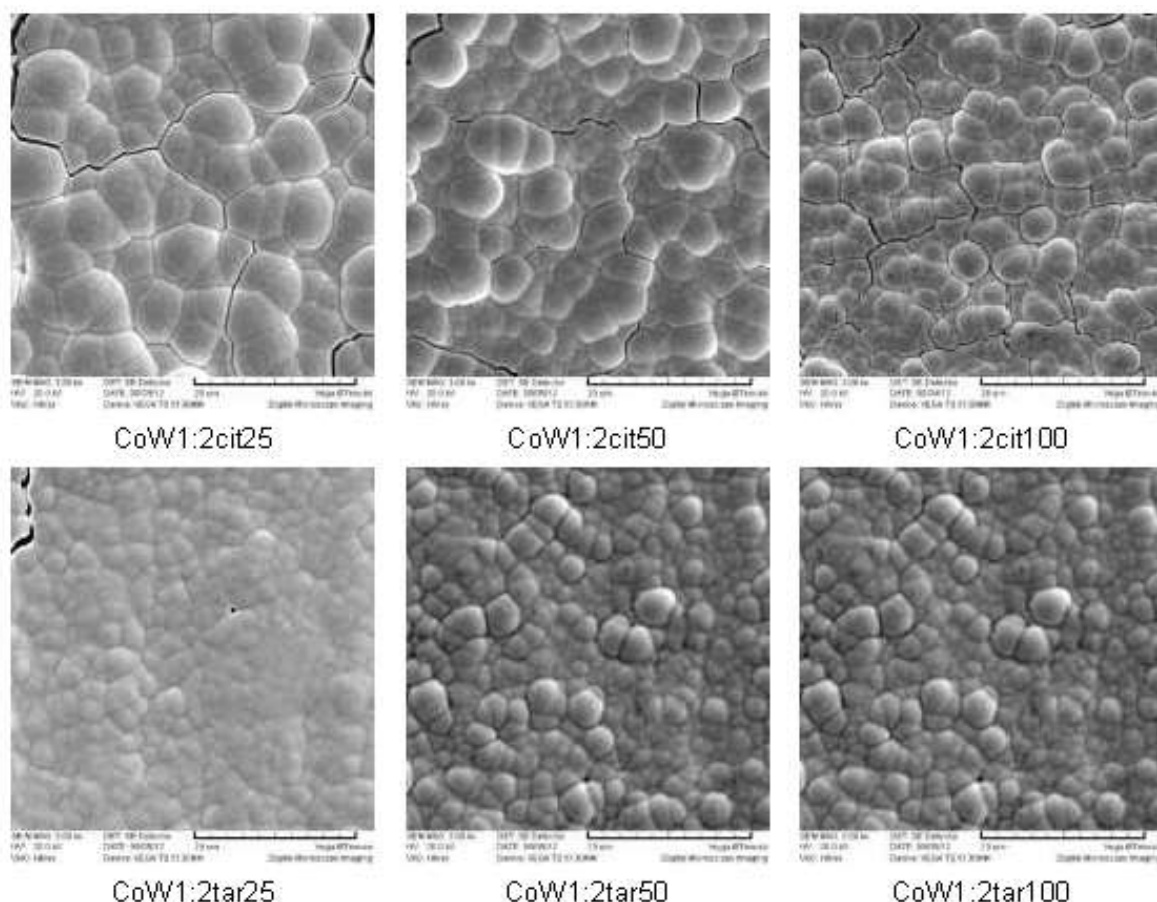


Figure 2. SEM photos of CoW electrodes at a magnification of $\times 3000$ - the influence of the deposition current density on the morphological characteristics of the coating

CONCLUSION

This study successfully synthesized Co and W-based coatings and evaluated their potential as catalysts for the Hydrogen Evolution Reaction (HER). The coatings were electrochemically deposited from citrate and tartrate baths onto a nickel substrate. All tested coatings exhibited superior catalytic activity compared to the pure nickel electrode, with the most active Co-W (CoW1:2tar100) electrode demonstrating an E_{300} value approximately 340 mV more positive.

The morphological characteristics and the electrocatalytic activity of the Co-W coatings were significantly influenced by the composition of the electrodeposition bath, the concentration of electroactive species, the bath pH value, and the applied deposition current density. Scanning Electron Microscopy (SEM) analysis revealed a nodular structure, which has a larger active surface compared to the pure nickel electrode. This attribute is of considerable importance due to its positive impact on the efficiency of electrolytic hydrogen production.

The observed increase in the activity of Co-W coatings can be attributed to both the true catalytic effect and the surface effect. Notably, all tested Co-W coatings were more active than pure Co coatings deposited under identical conditions from the same deposition baths without the presence of tungstate.

In conclusion, the Co and W-based coatings, particularly when obtained by electrochemical deposition from tartrate bath, demonstrated significant promise as catalysts for the Hydrogen Evolution Reaction due to their superior catalytic activity and enhanced active surface. Future investigations should focus on optimizing these deposition parameters and validating these findings in practical applications.

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