



Preparation and Characterization of Mixed Metal Oxides Coatings on Titanium Substrate

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Abstract

RuO₂-IrO₂-TiO₂ and RuO₂-IrO₂-TaO₂-TiO₂ are the most common mixed metal oxide (MMO) coatings coated on Ti substrates. MMO-coated titanium substrates serve as anodes in brine electrolyzers, which employ highly concentrated brine (33% NaCl) to generate chlorine gas and sodium hydroxide. These MMO electrodes were deposited using precursors that included ruthenium trichloride trihydrate (RuCl₃·3H₂O), diammonium iridium hexachloride [(NH₄)₂IrCl₆], tantalum pentachloride (TaCl₅), and titanium trichloride (TiCl₃). Highly effective RuO₂-IrO₂-TiO₂ and RuO₂-IrO₂-TaO₂-TiO₂ MMO coatings were achieved with the appropriate chemical composition. Both electrodes performed efficiently and showed high stability in the accelerated stability test, while tantalum in the coating composition enhances the MMO coating's stability.

Keywords: Chlorine evolution reaction (CER), Oxygen evolution reaction (OER), RuO₂-IrO₂-TiO₂, and RuO₂-IrO₂-TaO₂-TiO₂ MMO coatings

1. Introduction

The electrolysis of brine produces chlorine and sodium hydroxide, and it is regarded as one of the world's largest industrial electrolytic processes [1]. The vital role of chlorine and sodium hydroxide in the processing industries can be emphasized. Chlorine is required for the disinfection of drinking water [2], the production of polyvinyl chloride (PVC) [3], and the synthesis of a wide range of other chlorinated polymers, solvents, and specialty chemicals [4]. Sodium hydroxide is widely used in the pulp and paper industry [5], the extraction of aluminum from bauxite [6], clean-in-place systems in the food, beverage, and dairy sectors, and the creation of specialized chemicals [7]. Brine electrolyzer maintenance costs are a major factor affecting the chlor-alkali industry's profitability. The electrodes (anodes and cathodes) are critical components of every electrolyzer. Among the two electrodes, the anode takes more attention as it is subjected to failure much more than the cathode [8].

The brine electrolyzer consists of an anode and a cathode separated by a bipolar membrane [9]. Initially, graphite was utilized as an electrode. By the mid-1950s, commercial production of titanium, which has strong corrosion resistance, had advanced significantly in the USSR, the UK, and the United States. However, when polarized anodically in aqueous electrolytes, the metal soon produced a passive layer of titanium oxide. To efficiently employ the metal as an electrode, a stable, conductive

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coating has to be developed. To achieve this purpose, an adhesive layer of platinum on a titanium substrate was effectively electroplated, and the resulting electrode was swiftly brought to market for cathodic protection devices [10].

The first patent recognizing mixed metal oxide (MMO) coatings was submitted in 1965 and was awarded to Henri Beer [11]. The patent is principally concerned with the co-deposition of ruthenium and titanium oxides on a titanium substrate. The coating is applied as a paint comprising soluble compounds from the two metals, which are subsequently thermally degraded to generate an adhesive layer of mixed oxides [12]. The first MMO electrode to be successfully sold commercially was this RuO₂-TiO₂ coating on titanium. Later research revealed that the potentials for chlorine and oxygen evolution were determined by the quantity of ruthenium oxide in the coating.

Consequently, Henri Beer submitted a second patent (British Patent 1,195,871; 1967) 1967 that described a covering with less ruthenium oxide; this patent became known as Beer 2 [13]. This second-generation MMO electrode, less expensive than the Beer 1 anode but has comparable (if not greater) performance, has become the primary coating used in commercial chlorine cells [13]. Since the 1970s, MMO electrodes have altered the technological and economic aspects of producing chlorine, sodium chlorate, and sodium hypochlorite. Modifications to the Beer coating led to extended lives and lower prices. The effective development of membrane cell technology for large-scale chlorine and sodium hydroxide generation required further coating improvements. RuO₂ was partly replaced with IrO₂ to counteract the dissolution of the ruthenium oxide in the highly alkaline environment at the anode surface that can form in operating membrane cells [14].

In this study, ternary (RuO₂-TiO₂-IrO₂) and quaternary (RuO₂-TiO₂-IrO₂-TaO₂) MMO coatings were effectively fabricated on a Ti substrate. Each metal oxide plays a specific job. RuO₂ has the primary function of producing the electrocatalytic action. IrO₂ was employed to counteract the negative effects of oxygen gas evolution on electrode performance. Tantalum oxide was used in the coating instead of titanium oxide, which offered better-prolonged performance by limiting TiO₂ production at the coating/substrate contact [15]. TaO₂ was mixed with TiO₂ to improve the tolerance of manufactured MMO coatings to deterioration.

2. Experimental

MMO coatings were deposited using solutions including Ruthenium trichloride trihydrate (RuCl₃.3H₂O), diammonium iridium hexachloride [(NH₄)₂IrCl₆], tantalum pentachloride (TaCl₅), and titanium trichloride (TiCl₃), as mentioned in Table 1. Non-toxic and green solvents, such as water with the addition of hydrochloric acid, were employed to avoid more toxic and expensive alkoxides or organic solvents used in the sol-gel method, making our simple coating technique eco-friendly.

The Ti samples were coated as follows:

- Ti substrates were activated in an acidic solution at a sufficiently high temperature for an appropriate time.
- Activated samples were dipped in a coating precursor, dried, and heat-treated at a sufficiently high temperature.
- The coating process was repeated until the desired coating weight was achieved. The minimum required coating weight is 0.2 mg/cm² (2 g/m²).

Table 1: MMO coating bath composition

Bath no.	Molar Conc. of Precursors	Content of RuCl ₃ .3H ₂ O g/100 ml	Content of [(NH ₄) ₂ IrCl ₆] g/100 ml	Content of TaCl ₅ g/100 ml	Content of TiCl ₃ g/100 ml	Molar ratio of Proposed MMO
Bath 1	0.1M	1.5694	0.4410	---	0.4627	60% RuO ₂ -30% TiO ₂ -10% IrO ₂
Bath 2	0.1 M	1.5694	0.6615	0.1791	0.3085	60% RuO ₂ -20% TiO ₂ -15% IrO ₂ -5% Ta ₂ O ₅

- The coating weight was calculated by subtracting the weight of the activating sample from the weight of the coated sample.
- The surface morphology and thickness of the MMO coatings were analyzed using the field emission scanning electron microscope (FE-SEM). Whereas the chemical composition of the MMO coatings was determined using the electron dispersive spectroscopy (EDS) unit attached to the SEM.
- The adhesion strength of the MMO coatings was assessed using the adhesion tape testing method (Hatch cutter test) [16]. This test is a simple identification that evaluates the adherence between the coating layer and substrate by applying and removing pressure-sensitive tape over "X" cuts made using Elcometer Cross Hatch Cutter in the coating film. The test results were categorized into six grades as follows:
 - 5A: no removal or peeling.
 - 4A: Trace peeling or removal along incisions.
 - 3A: Jagged removal along incisions up to 1.6 mm on either side.
 - 2A: Jagged removal along incisions up to 3.2 mm on either side.
 - 1A: Removal from most of the area of the X under the tape.
 - 0A: Removal beyond the area of the X.
- The electrochemical efficiency of MMO coatings was evaluated using the current interrupting technique, which is often used in assessing electrolyzer anodes in the industry. The MMO-coated samples were pre-polarized for 10 minutes at 50°C with $3 \text{ kA} / \text{m}^2$ ($0.3 \text{ A}/\text{cm}^2$) to activate the electrode and to put the coating into a stable electrochemical condition. After 10 minutes, the current is shut off. The resultant angle following the potential drop must be around 90 degrees. The bigger the resultant angle following the voltage drop, the greater the effect on the electrode's performance.
- The stability of the deposited electrodes was further evaluated utilizing chronopotentiometry using an accelerated stability test (AST) in an acidified brine solution (5 M NaCl miscible with 0.01 M HCl, pH 2) at a current density of $1 \text{ A}/\text{cm}^2$ [17]. The two electrochemical experiments were carried out using an autolabpotentiostat/galvanostat powered by NOVA, with a three-electrode cell including a calomel electrode as the reference electrode, a platinum sheet as the counter electrode, and MMO-coated substrates as the working electrode.

3. Results and Discussion

Figure 1 displays a macroscopic analysis of the $\text{RuO}_2\text{-IrO}_2\text{-TiO}_2$ and $\text{RuO}_2\text{-IrO}_2\text{-TaO}_2\text{-TiO}_2$ MMO coatings on titanium substrates. The black surfaces of the two samples indicate that the MMO coating was effectively applied to the titanium substrates. Table 2 shows the MMO coating weights for $1.97 \text{ mg}/\text{cm}^2$ of $\text{RuO}_2\text{-IrO}_2\text{-TiO}_2$ and $4.8 \text{ mg}/\text{cm}^2$ of $\text{RuO}_2\text{-IrO}_2\text{-TaO}_2\text{-TiO}_2$ are obtained.

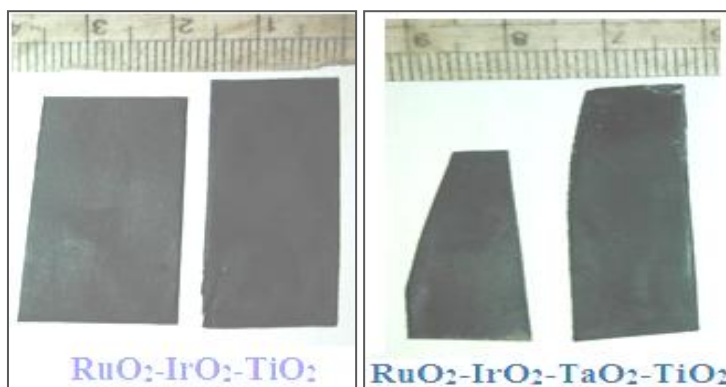


Figure 1: Macrographs of coated samples

Table 2: Amount of (a) RuO₂-IrO₂-TiO₂ and (b) RuO₂-IrO₂-TaO₂-TiO₂ MMO coated on titanium substrate

	Wt. before (g)	Wt. after (g)	Wt. gain (g)	Area (Cm ²)	Wt./area (mg/cm ²)
(a)	2.2468	2.2665	0.0197	11	1.8
(b)	1.1998	1.2274	0.0276	5.75	4.8

Figures 2a and 3a show SEM micrographs of the MMO-coated samples. MMO coatings evenly coated the surface. Both RuO₂-IrO₂-TiO₂ and RuO₂-IrO₂-TaO₂-TiO₂ MMO coatings are compact and have few voids in their microstructures. The EDS spectra of the produced RuO₂-IrO₂-TiO₂ and RuO₂-IrO₂-TaO₂-TiO₂ MMO coatings (Figures 2b & 3b) showed that the coatings composition was 48.3wt% RuO₂-8.48wt% IrO₂- 43.21wt% TiO₂ and 54.93wt% RuO₂-8.65wt% IrO₂- 2.94wt% TaO₂- 33.47wt% TiO₂. the percentage of Ti, Ru, Ir and Ta oxides were calculated based on the weight %

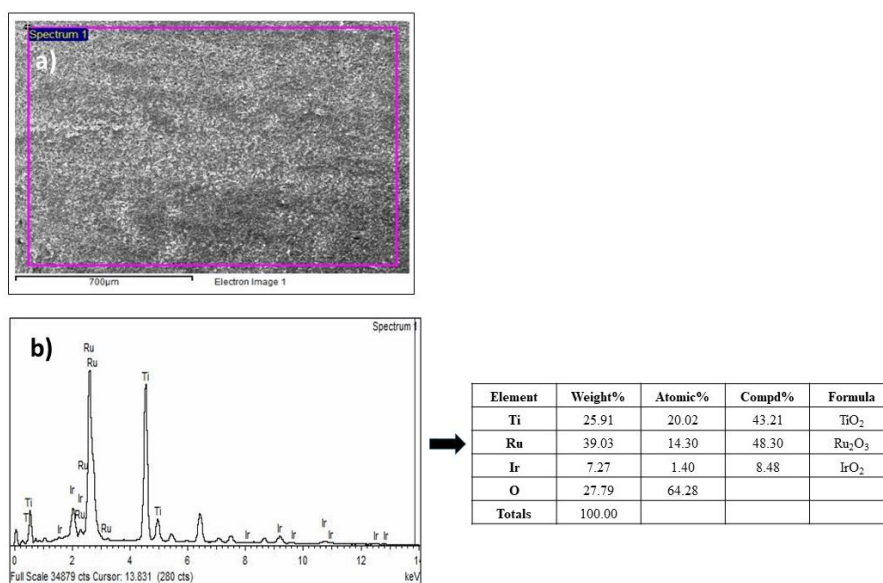
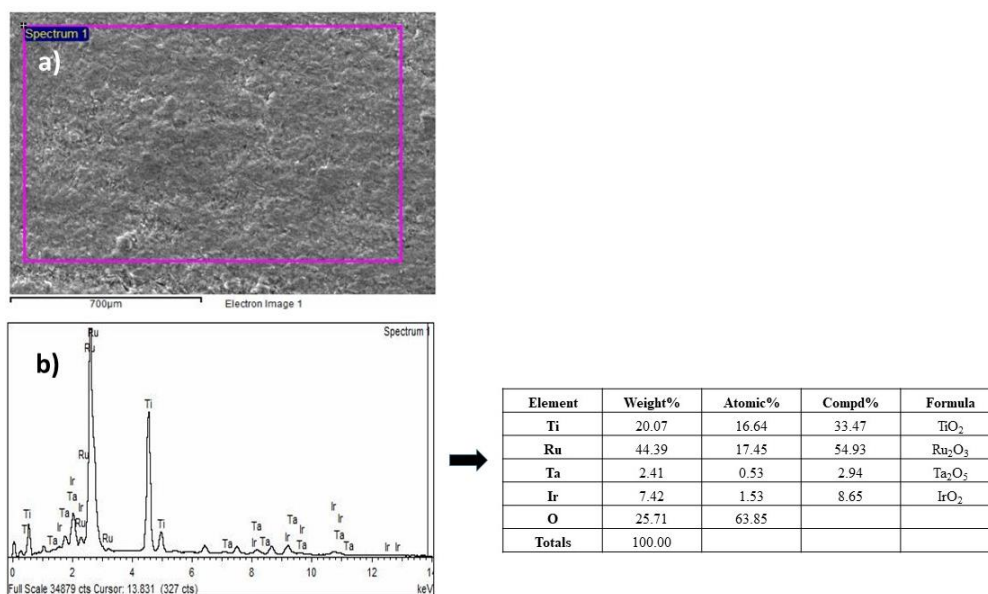
**Figure 2:** a) SEM micrograph and b) EDS of RuO₂-IrO₂-TiO₂ MMO coating sample**Figure 3:** a) SEM micrograph and b) EDS of RuO₂-IrO₂-TaO₂-TiO₂ MMO coating sample

Figure 4 depicts SEM images of the cross sections of titanium substrates coated with $\text{RuO}_2\text{-IrO}_2\text{-TiO}_2$ and $\text{RuO}_2\text{-IrO}_2\text{-TaO}_2\text{-TiO}_2$. Compact layers of MMO coating were seen in each sample. The same coating thickness in both samples indicates a uniform dispersion of the deposited MMO on the titanium substrates. The $\text{RuO}_2\text{-IrO}_2\text{-TaO}_2$ coating has a measured thickness of 18 μm , whereas $\text{RuO}_2\text{-IrO}_2\text{-TaO}_2\text{-TiO}_2$ has a substantially greater thickness of 114 μm . These findings are consistent with the estimated weight gain in Table 2, demonstrating that Ta addition to the coating solution promotes MMO deposition.

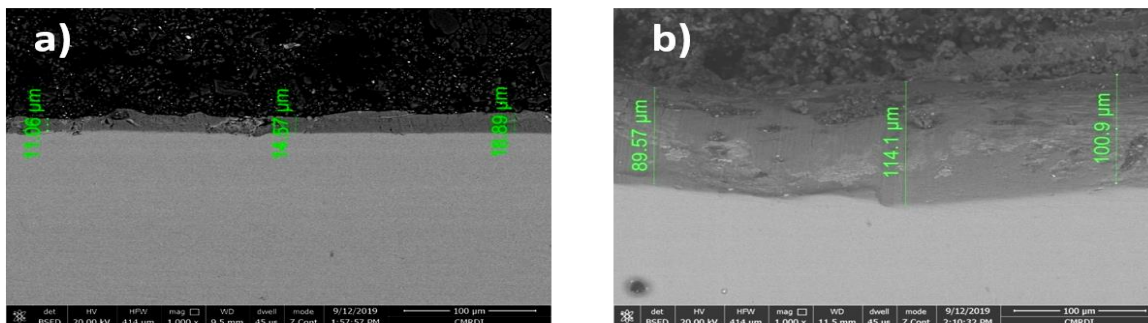


Figure 4: SEM of the cross-section of Ti substrate coated with a) $\text{RuO}_2\text{-IrO}_2\text{-TiO}_2$ and b) $\text{RuO}_2\text{-IrO}_2\text{-TaO}_2\text{-TiO}_2$ MMO

Figure 5 depicts the MMO adhesion test results, which show that MMO coatings adhere effectively to the titanium substrate without peeling. According to the adhesion test standard, MMO coatings are classed as 4A, which indicates trace peeling or removal along incisions.

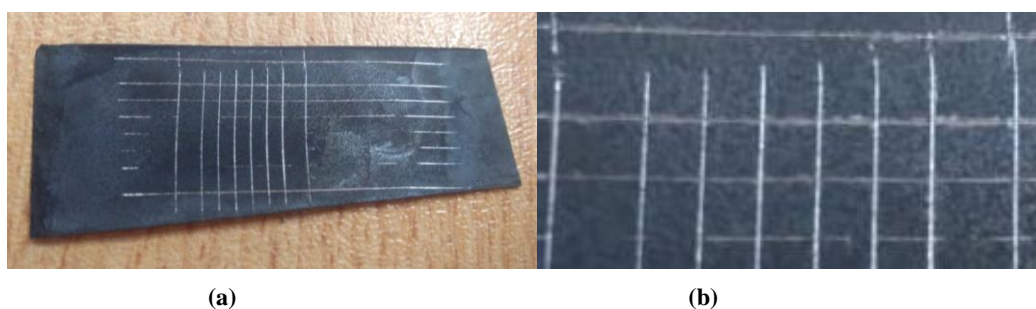


Figure 5: Adhesion test of Ti substrate coated with a) $\text{RuO}_2\text{-IrO}_2\text{-TiO}_2$ and b) $\text{RuO}_2\text{-IrO}_2\text{-TaO}_2\text{-TiO}_2$ MMO. The electrochemical efficiency of the deposited MMO on titanium substrates in brine solution was determined using the current on-off test. The MMO-coated electrode was pre-polarized at a current density of 3 kA/m^2 (0.3 A/cm^2), which is the actual value used in the chlor-alkali industry. The current was then stopped, and the angle at the potential drop was calculated. The tilt should be almost 90° to ensure adequate MMO coating deposition. Figure 6 depicts the results of the electrochemical efficiency tests on the MMO-coated samples. The resultant angle following the potential drop is about 90 degrees, suggesting the creation of flawless coatings. The potential in the active state is almost the same with slight oscillation in both electrodes, also indicating a high efficiency of MMO coat performance in the case of $\text{RuO}_2\text{-IrO}_2\text{-TiO}_2$ and $\text{RuO}_2\text{-IrO}_2\text{-TaO}_2\text{-TiO}_2$ as well.

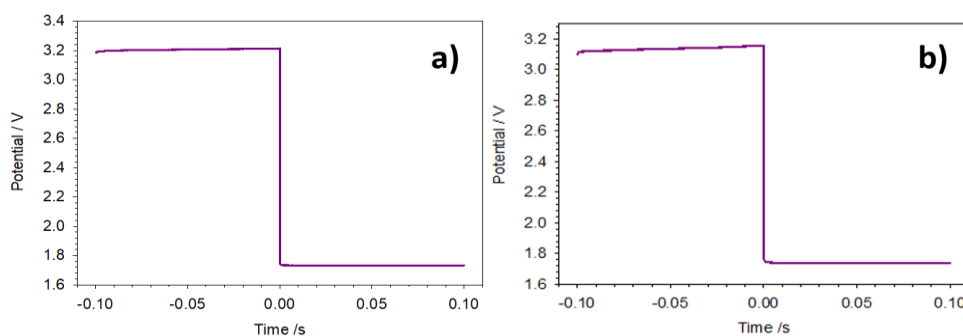


Figure 6: Electrochemical efficiency test of a) $\text{RuO}_2\text{-IrO}_2\text{-TiO}_2$ and b) $\text{RuO}_2\text{-IrO}_2\text{-TaO}_2\text{-TiO}_2$ MMO

The accelerated stability test (AST) results for both MMO coatings are given in Figure 7. The lack of quick breakdown in the voltage of these anodes reveals their exceptional stability. The observed steady reduction in potential over the first 20-30 minutes for the RuO₂-IrO₂-TiO₂ and RuO₂-IrO₂-TaO₂-TiO₂ MMO electrodes may be attributed mostly to the partial breakdown of the less stable anodized layer that developed on the coating's outer surface. The catalytic efficiency of both electrodes appears to have remained largely steady during the 120-minute testing period. The addition of both IrO₂ and IrO₂/TaO₂ in the ternary and quaternary electrodes enhances the stability of the electrode. Steady-state potentials (E_{ss} , in V vs. SCE) of 3.76 and 3.96 V are observed for the RuO₂-IrO₂-TiO₂ and RuO₂-IrO₂-TaO₂-TiO₂, respectively.

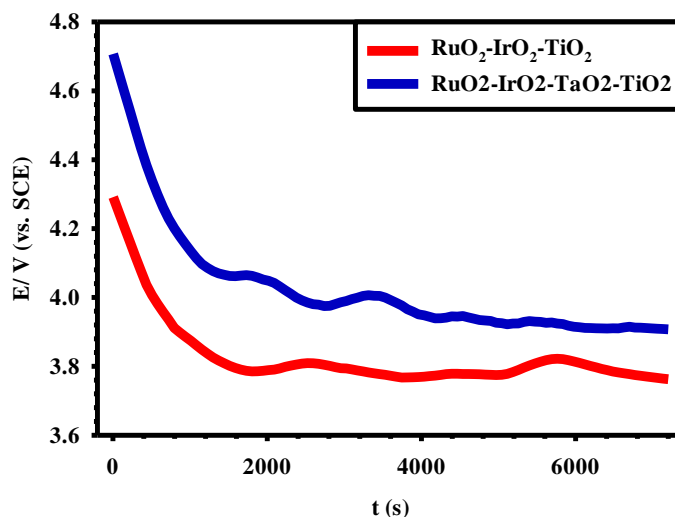


Figure 7: Accelerated stability test (AST) at a current density of 1 A/cm² for a) RuO₂-IrO₂-TiO₂ and b) RuO₂-IrO₂-TaO₂-TiO₂ MMO in 5 M NaCl + 0.01 M HCl brine solution of pH 2

The major effective chemical processes in concentrated brine are the cathodic hydrogen evolution reaction (HER) and the anodic chlorine evolution reaction (CER), which are detailed in the following two Eqs. 1 and 2, respectively [18]:



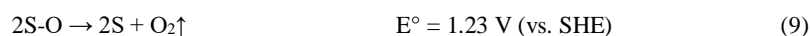
Thus, the net reaction is described by Eq. 3 [19]:



The CER takes place in two stages. In the first, the chloride ion adsorbs on the substrate's surface-active site (S), such as RuO₂, and oxidizes as described in Eq. 4. After that, the adsorbed chloride ion reacts with a dissolved chloride ion or another adsorbed chloride ion to generate chlorine gas, as shown in Eqs. 5 and 6 [20]:



At high pH, oxygen evolution becomes the dominant anodic reaction, and ruthenium dioxide is oxidized to a soluble ruthenium compound (RuO₄) and removed from the electrode surface [21]. The concentration of chloride ions lowers with time, allowing the OER to compete against the CER. The degradation of water in acidic situations serves as an example for analyzing the OER. This process entails many chemical processes on the surface-active sites, as shown in Eqs. 7-9 [22].



As described in our previous work [22], each metal oxide was added to the coating mixture to perform a specific role. In this technique, RuO₂ was the most essential component in electrocatalytic performance, while IrO₂ was used to polarize the OER to a more negative potential than the CER potential, and TaO₂ was blended with TiO₂ to increase the corrosion resistance and enhance coating stability. Valve metals, such as tantalum, enable electricity to flow in one way. They usually form an extremely resistant thin oxide coating on their surfaces when anodic conditions are met, which allows them to function as a cathode rather than an anode in a galvanic cell.

The economic impact of the present work is highly guaranteed. To clarify the matter, an example predicting the cost of coating a brine electrolyzer anode used actually in the chlor-alkali plant is illustrated. An anode with an area = 1.7 m² is required to be MMO coated so that the coating load is 5 g/m². Consequently, the coating load over the entire anode area will be 8.5 g. If we suppose that another 1.5 g is lost during the coating process, then the total MMO coating load will be 10 g/1.7 m². The cost of chemicals is calculated based on the hypothesis that MMO coating composition is: TiO₂(20%)/RuO₂(50%)/IrO₂(15%)/Ta₂O₅(5%), accordingly, 2 g TiO₂, 5 g RuO₂, 1.5 g IrO₂, 0.5 g Ta₂O₅ are needed. The total cost for chemicals is = 106 \$ ≈ 5300 LE. Adding the same amount as the manufacturing cost, the total cost will be 10600 LE. The cost of performing the coating process abroad is about 70,000 LE which is almost seven times more than the cost of the proposed developed method.

Regarding the scalability; the present MMO coating technology is not complicated and can be applied on Large-area electrodes. A workshop has been attached and established for this purpose.

4. Conclusions

Based on the findings of the present study, the following conclusions may be drawn:

- Highly effective RuO₂-IrO₂-TiO₂ and RuO₂-IrO₂-TaO₂-TiO₂ MMO coatings with suitable chemical composition were produced.
- RuO₂-IrO₂-TaO₂-TiO₂ MMO coating has a higher weight gain and higher coating thickness compared to RuO₂-IrO₂-TiO₂.
- EDS analysis confirmed that the chemical compositions of the prepared MMO coatings are comparable to those utilized in the field.
- The adhesion test showed that both MMO coatings well adhered to the titanium substrate.
- The addition of IrO₂ increases the electrochemical efficiency of MMO electrodes, whereas TaO₂ improves corrosion resistance.

5. Acknowledgments

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6. Competing interests

The authors declare no competing interests.

7. References

1. M. Reig, S. Casas, C. Aladjem, C. Valderrama, O. Gibert, F. Valero, C.M. Centero, E. Larrotcha, J.L. Cortina, "Concentration of NaCl from seawater reverse osmosis brines for the chlor-alkali industry by electrodialysis", *Desalination*, 342, (2014), 107-117. <https://doi.org/10.1016/j.desal.2013.12.021>
2. M. Jin, L. Liu, D.N. Wang, D. Yang, W.L. Liu, J. Yin, Z.W. Yang, H.R. Wang, Z.G. Qui, Z.Q. Shin, D.Y. Shi, H.B. Li, J.H. Guo, and J.W. Li, "Chlorine disinfection promotes the exchange of antibiotic resistance genes across bacterial

- genera by natural transformation”, *The ISME journal*, 14(7), (2020), 1847-1856. <https://doi.org/10.1038/s41396-020-0656-9>
3. S. Kumagai, J. Lu, Y. Fukushima, H. Ohno, T. Kameda, and Yoshioka, “Diagnosing chlorine industrial metabolism by evaluating the potential of chlorine recovery from polyvinyl chloride wastes—A case study in Japan”, *Resources, Conservation and Recycling*, 133, (2018), 354-361. <https://doi.org/10.1016/j.resconrec.2017.07.007>
 4. T. Yang, K.Y. Wang, and T.S. Chung, “Fabrication of thin-film composite hollow fiber membranes in modules for concentrating pharmaceuticals and separating sulphate from high salinity brine in the chlor-alkali process”, *Journal of Membrane Science*, 640, (2021), 119822. <https://doi.org/10.1016/j.memsci.2021.119822>
 5. D. Mboowa, “A review of the traditional pulping methods and the recent improvements in the pulping processes”, *Biomass Conversion and Biorefinery*, 14(1), (2024), 1-12. <https://doi.org/10.1007/s13399-020-01243-6>
 6. R. Fu, H. Wang, J. Yan, R. Li, B. Wang, C. Jiang, Y. Wang, and T. Xu, “Ion-injection bipolar membrane electrodialysis realizes 8+ mol/L caustic soda conversion from the brine stream.”, (2023). <https://doi.org/10.21203/rs.3.rs-2494244/v1>
 7. G. Mamo, and B. Mattiasson, “Alkaliphiles: The versatile tools in biotechnology”, *Alkaliphiles in Biotechnology*, (2020), 1-51. https://doi.org/10.1007/10_2020_126
 8. I. Requena-Leal, M. Carvela, C.M. Fernández-Marchante, J. Lobato, and M.A. Rodrigo, “On the use of chlor-alkali technology to power environmental electrochemical treatment technologies”, *Current Opinion in Electrochemistry*, (2024), 101461. <https://doi.org/10.1016/j.coelec.2024.101461>
 9. S. Mohammadi, and T. Ebadi, “Production of a water disinfectant by membrane electrolysis of brine solution and evaluation of its quality change during the storage time”, *Arabian Journal of Chemistry*, 14(2), (2021), 102925. <https://doi.org/10.1016/j.arabjc.2020.102925>
 10. J. Aromaa and O. Forsen, “Evaluation of the electrochemical activity of a Ti–RuO₂–TiO₂ permanent anode”, *Electrochimica Acta*, 51, (2006), 6104–6110. <https://doi.org/10.1016/j.electacta.2005.12.053>
 11. S.F. Mirseyed, K. Jafarzadeh, A. Rostamian, A. Semnani, H.M. Abbasi, and M. Ostadhassan, “A novel approach to the role of iridium and titanium oxide in deactivation mechanisms of a Ti/(36 RuO₂-x IrO₂-(64-x) TiO₂) coating in sodium chloride solution”, *Corrosion Science*, 206, (2022), 110481. <https://doi.org/10.1016/j.corsci.2022.110481>
 12. A.R. Zeradjanin, F.L. Mantia, J. Masa, and W. Schuhmann, “Utilization of the catalyst layer of dimensionally stable anodes—Interplay of morphology and active surface area”, *Electrochimica Acta*, 82, (2012), 408-414. <http://dx.doi.org/10.1016/j.electacta.2012.04.101>
 13. T.F. O’Brien, T.V. Bommaraju, and F. Hine, “History of the chlor-alkali industry”, *Handbook of Chlor-Alkali Technology*, (2005), 17-36.
 14. Z. Yi, C. Kangning, W. Wei, J. Wang, and S. Lee, “Effect of IrO₂ loading on RuO₂–IrO₂–TiO₂ anodes: A study of microstructure and working life for the chlorine evolution reaction”, *Ceramics International*, 33, (2007), 1087–1091. <https://doi.org/10.1016/j.ceramint.2006.03.025>
 15. J. Xu, W. Hu, S. Xu, P. Munroe, and Z. Xie, “Electrochemical Properties of a Novel β-Ta₂O₅ Nanoceramic Coating Exposed to Simulated Body Solutions”, *ACS Biomaterials Science & Engineering*, 2(1), (2016) 73-89. <https://doi.org/10.1021/acsbiomaterials.5b00384>
 16. L. Liverani, J.A. Roether, P. Noeaid, M. Trombetta, D.W. Schubert, and A.R. Boccaccini, “Simple fabrication technique for multilayered stratified composite scaffolds suitable for interface tissue engineering”, *Materials Science and Engineering: A*, 557, (2012), 54-58. <https://doi.org/10.1016/j.msea.2012.05.104>

17. A.B. Abdel-Aziz, F.E.T. Heakal, R.M. El Nashar, and I.M. Ghayad, "Green synthesis and characterization of binary, ternary, and quaternary Ti/MMO anodes for chlorine and oxygen evolution reactions", *Scientific Reports*, 14(1), (2024), 9821. <https://doi.org/10.1038/s41598-024-59595-2>
18. M. Jiang, H. Wang, Y. Li, H. Zhang, G. Zhang, Z. Lu, X. Sun, and L. Jiang, "Superaerophobic RuO₂-Based Nanostructured Electrode for High-Performance Chlorine Evolution Reaction", *Small*, 13(4), (2017) 1602240. <https://doi.org/10.1002/sml.201602240>
19. H. Over, "Atomic scale insights into electrochemical versus gas phase oxidation of HCl over RuO₂-based catalysts: A comparative review", *Electrochimica Acta*, 93 (2013) 314-33. <http://dx.doi.org/10.1016/j.electacta.2012.12.099>
20. B.E. Conway, G. Ping, A.D. Battisti, A. Barbieri, and G. Battaglin, "Behaviour of the Adsorbed Cl⁻ Intermediate in Anodic Cl₂ Evolution at Thin-film RuO₂ Surfaces", *Journal of Materials Chemistry*, 1(5) (1991) 725-34. <https://doi.org/10.1039/JM9910100725>
21. L.D. Burke, O.J. Murphy, J.F. O'Neill, and S. Venkatesan, "The Oxygen Electrode Part 8.-Oxygen Evolution at Ruthenium Dioxide Anodes", *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 73, (1977) 1659-71. <https://doi.org/10.1039/F19777301659>
22. G. Lodi, E. Sivieri, A.D. Battisti, and S. Trasatti, "Ruthenium dioxide-based film electrodes. III. Effect of chemical composition and surface morphology on oxygen evolution in acid solutions", *Journal of Applied Electrochemistry*, 8(2) (1978) 135-43. <https://doi.org/10.1007/BF00617671>.