

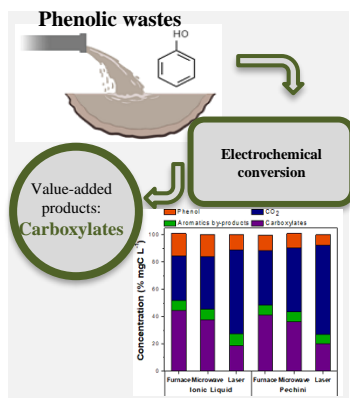
New MMO coatings for electro-refinery applications: Promoting the production of carboxylates

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This study explores the circular economy by assessing mixed metal oxide (MMO) anodes, made of ruthenium and antimony, for electrochemical organic refining. Phenol solutions were oxidized to convert phenolic residues into valuable carboxylates for electrosynthesis or fuel. MMO anodes were synthesized via two methods: Pechini and ionic liquid (IL), and subjected to three heating treatments: oven, microwave, and CO₂ laser. Notably, laser-treated IL anodes exhibited exceptional stability due to an insulating TiO₂ layer, despite suboptimal catalytic properties. This research underscores the significance of coating variations with identical compositions, contributing to the advancement of sustainable electrochemical technologies for organic waste treatment.

Introduction

The increase in studies that improve new approaches to treat water contaminated with organic compounds, using organic electrorefining with a focus on conversion into high value-added products, has been increasingly observed. Electrochemical processes stand out for their efficient action in converting organic molecules into valuable molecular products. To ensure 100% efficiency in the electrochemical process, the anode plays a prominent role. Mixed metal oxide (MMO) anodes are a reference in the literature for the treatment of contaminated water due to the efficient generation of hydroxyl radicals [1]. Anode synthesis technologies have been increasingly investigated to improve their physical and electrochemical properties. Among them, microwave and CO₂ laser technologies have gained prominence, offering advantages such as fast processing times, rapid heating and cooling rates, and ease of parameter optimization [1]. Although many studies report the efficiency of applying MMO anodes in the degradation of organic contaminants, studies exploring the impact of different synthesis routes on electrocatalytic properties and the conversion of contaminants into value-added products are scarce [2]. This study aims to evaluate the durability of Ti/RuO₂-Sb₂O₄ anodes synthesized through the ionic liquid and polymer precursor methods for long-term operation of electrochemical technologies, generating carboxylate acids through phenol oxidation in a novel electrochemical flow reactor.

Material and Methods

MMO anodes, composed of Ti/(RuO₂)₈₀(SbO₂)₂₀, were fabricated using the classical thermal decomposition of polymeric precursors method and the dipropyl ammonium butyrate (DPA-Bu) ionic liquid [3]. Three different heating techniques were employed: furnace, CO₂

laser (model GEM- 100 L – Coherent, and hybrid microwave heating (Consul brand). The accelerated life tests were conducted with continuous stirring while applying a current density of 100 mA cm⁻². The electrolysis experiments used 100 mL of a synthetic solution containing 300 mg L⁻¹ of phenol, 3 g L⁻¹ of NaOH, and 3 g L⁻¹ of Na₂SO₄ in the flow reactor, applying a current density of 100 mA cm⁻² over 8 hours. The removal of phenol was quantified using high-performance liquid chromatography (HPLC) Shimadzu, with a Shimadzu UFLC-20 system coupled to a UV detector and for analyzing short-chain intermediates, a Hplex H reversed-phase column was used. All samples of short-chain intermediates were acidified to a pH of approximately 4 to turn carboxylates into carboxylic acids for quantification purposes.

Results and Discussion

Scanning electron microscopy images of the anode surfaces reveal that, regardless of the synthesis method, anodes calcined in the furnace and microwave exhibit a "cracked mud" morphology. The anodes calcined using the laser method display a more compact structure with fewer visible cracks. These surface features are attributed to differences in the thermal expansion coefficients between the substrate and the coating, leading to mechanical stress. All electrodes demonstrate nearly equivalent electrochemically active areas. Notably, anodes processed using CO₂ laser exhibit a larger surface area. Laser-prepared anodes exhibit a higher voltammetric charge compared to those produced by microwave and furnace methods. Although the choice of solvent has a less significant impact, anodes prepared with ionic liquid exhibit slightly higher voltammetric charges, as observed in previous studies that reported larger voltammetric areas for MMOs prepared using microwave and laser heating.

Service lifetime varied with heat treatment methods and precursor solutions, with stability following the sequence: laser > microwave > furnace. Besides, Anodes synthesized with ionic liquid demonstrated greater durability than those made using the Pechini Method, as depicted in Figure 1a. The Figures 1b-c showed a general decrease in activity towards oxygen evolution, with minimal reduction in voltammetric charge, particularly in furnace-prepared anodes. In Figure 1d it was possible to observe the voltammetric charge of these anodes varied by around 20.5–25.5% post-deactivation, maybe due both erosion and passivation by TiO_2 interlayer. Was analyzed the degradation trend of phenol and the evolution of its primary reaction intermediates during electrooxidation of a phenol solution (300 mg L^{-1}) at a current density of 100 mA cm^{-2} , using the $\text{Ti/RuO}_2\text{-Sb}_2\text{O}_4$ anode fabricated with ionic liquid and Pechini method as the solvent and furnace, microwave, CO_2 heating. In general, the main reaction intermediates in the electrochemical oxidation of phenol using $\text{Ti/RuO}_2\text{-Sb}_2\text{O}_4$ anodes are carboxylates, including oxalate, malonate, maleate, succinate, formate, acetate, and propionate, with oxalate, maleate, and malonate being the predominant species. This is the expected result, considering the refractory character of oxalate and maleate, which facilitates their accumulation in the system. Aromatic compounds such as benzoquinone and hydroquinone are also formed but are present in lower concentrations. Among the tested electrodes, furnace-heated anodes exhibit superior performance in the formation and accumulation of carboxylates, with

percentages of 45 and 41% for IL and Pechini methods, respectively. Electrolysis using furnace-heated electrodes results in the highest accumulation of carboxylates, particularly with the IL method: 188.5 mg L^{-1} of oxalate, 110 mg L^{-1} of malonate, and 90 mg L^{-1} of maleate.

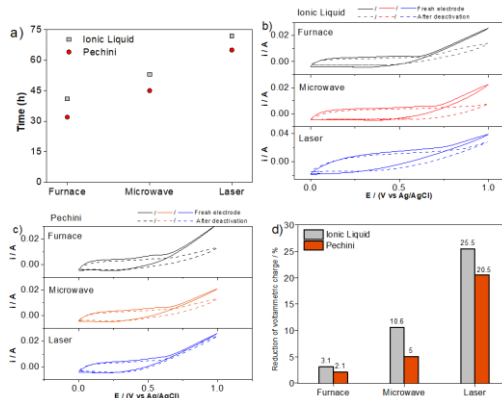


Figure 1.

a) Service lifetime of electrodes prepared using the ionic liquid and Pechini methods. b) Voltammetric curves of ionic liquid-prepared anodes before (solid line) and after (dashed line) the service lifetime tests. c) Voltammetric curves of Pechini-prepared anodes before (solid line) and after (dashed line) the service lifetime tests. d) Reduction in voltammetric charge of the electrodes following the service lifetime tests.

Conclusions

This study marks a significant step toward the development of more efficient and sustainable electrochemical treatment technologies for organic compounds. The electrode with the longest service life did not demonstrate the most effective catalytic properties for minimizing mineralization, however the anodes prepared using electric furnace were more effective in forming and accumulating carboxylates and exhibited the lowest degree of mineralization, typically around 40–45%. The observed variations in the coatings, despite having identical chemical compositions, underscore the importance of ongoing research in this area.

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