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ETRI 2023

BOOK OF ABSTRACTS

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Methodology: The methodological approach of this article consists of proposing a Neural Network model for segmenting images of wind turbine blades. The model is trained and tested on a dataset of images captured and provided from a wind farm by through drones. Before training, the images are manually annotated at the pixel level and converted to grayscale, the pixel values representing the background and the turbine blade, respectively. The data set consists of a bank of images of wind turbine blades, and were separated into training, having their masks labeled, and test, comprising 35% of the total images provided. To improve segmentation accuracy and reduce computational complexity, the Neural Network (U-Net) model uses depth-wise separable convolution and fusion of batch convolution and normalization layers. Furthermore, the model employs a residual neural network (ResNet) as a backbone for feature extraction and attention mechanisms to capture important details in images. Experimental results show that the improved U-Net outperforms other segmentation methods in terms of average intersection over union and average pixel accuracy. Furthermore, the model has a faster execution time compared to other models.

Preliminary results: Project still in progress, so there are no results yet.

Preliminary conclusions: Project still in its initial phase, so no conclusions at the moment.

0911 – BECCUS13 (TV2)

Chairs: André Dourado – Marcos Buckeridge

Thiago Vasconcelos de Barros Ferraz
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Abstract Title: Enabling ethanol electro-oxidation in seawater-like electrolytes for energy conversion and CO2 mitigation

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Abstract: The global temperature increases and alarming climate occurrences led 195 nations to sign the Paris Climate Agreement in 2015, committing to limit global warming to 1.5 °C - 2 °C by 2100. Achieving this goal requires fast decarbonization of key productive sectors by 2050 and subsequent active removal of 10-20 Gt of atmospheric CO2 annually. Among the existing mitigation alternatives, a promising one involves adapting the rapidly expanding desalination infrastructure worldwide for the parallel electrochemical capture and mineralization of CO2 into chemically stable CaCO3 and MgCO3 salts - which can be safely stored in the seafloor for hundreds to thousands of years. Many thermodynamic/technic constraints associated with the use of the of hydrogen oxidation (HOR, E° = 0 V vs. RHE) or oxygen evolution reactions (OER, E° = 1.23 V vs. RHE) as half-cell anodic reactions in support systems for such application have been overcome with some success in the field of fuel cells by replacing them with the oxidation of biomass-based low molecular weight aliphatic alcohols – which tend to exhibit comparatively modest thermodynamic oxidation potentials (<0.5 V vs. RHE). Nonetheless, the Cl- anions in seawater (~0.56 M) are already well-known to cause the poisoning of transition metal-derived electrodes for organic compound oxidation, even in trace amounts at acid and neutral pH conditions. Herein we report on the seawater-like electrolytes alkalization as a way to enhance the feasibility of ethanol oxidation in such naturally chlorine-rich media. Polycrystalline platinum was chosen as model catalyst to be used in a three-electrode cell and an ethanol concentration of 1 M was maintained throughout the measurements. The potentiodynamic polarization tests indicated an enhancement in the current densities of the ethanol anodic processes with increasing pH values - consistent with a decrease in the specific adsorption strength of the Cl- anions on the Pt surface - reaching up to 3 mA cm-2 at 0.69 V (vs. RHE) in a solution with a non-depleted chloride level of 0.5 M and pH of 14. Furthermore, the aforementioned adjustment of the experimental parameters allowed us to access dynamic instabilities in the form of potential oscillations – which otherwise do not appear in the purely representative environmental near-neutral pH of 8.2 - and that can be, in principle, harnessed to improve the power density delivered by electrochemical devices operating under the proposed conditions.

Keywords: Electrocatalysis, Seawater, Ethanol Electro-oxidation, Dynamic Instabilities.

Introduction and Objectives: The noticeable increase of the average global temperature in recent decades – and the coincident occurrence of alarming climate events – led in 2015 to 197 nations to sign the Paris Accord, in which they committed to take part in a joint effort to limit the global warming to 1.5 °C – 2 °C (above the pre industrial levels) by 2100. However, in order for this goal to be achieved, not only a fast decarbonization of the key productive sectors of the economy is required to happen by 2050; around 10 – 20 Gt of atmospheric CO2 will also need to be actively removed and safely immobilized every year from that point forward. Among the various groups of alternatives under evaluation (e.g., DAC and BECCUS), those proposing the use of the oceans – the largest natural carbon sink known – are receiving growing attention since they are the only ones capable of tackling the scale of the challenge. One of the most promising involves adapting the rapidly expanding desalinization infrastructure around the world with parallel electrochemical processes able to capture the CO2 and mineralize it in the form of chemically stable CaCO3 and MgCO3 salts – which can be harmlessly stored in the seafloor during hundreds to thousands of years. A major conceptual energy limitation of the previous approach resides in the intrinsic overpotentials required for the electrochemical device to operate with significant current densities. Usually, water oxidation or hydrogen oxidation are applied as the anodic half-cell reaction on such devices, though the former suffers from the lack of efficient, stable and commercially available catalysts, and the gas diffusion anodes required by the latter are still on the course of being adequately scaled up. Such difficulty has been circumvented with a good degree of success in the field of fuel-cells by replacing the oxygen evolution reaction (OER, E° = 1.23 V vs. RHE) and the hydrogen evolution reaction (HER , E° = 0 V vs. RHE) with the oxidation of biomass-based low molecular weight aliphatic alcohols (e.g., methanol, ethanol, glycerol) – which tend to exhibit comparatively modest thermodynamic oxidation potentials (~0.10 V vs. RHE). Nonetheless, an important aspect to consider is that seawater possesses extremely high Cl- concentration (around 0.56 M), which has been long well reported to poison the surface of most transition metal-derived electrodes to organic compounds oxidation in general, even in trace amounts in acidic and neutral media. In light of the exposed, in this work, we approached the alkalinization of seawater-like electrolytes as means of increasing the energetic and economic feasibility of applying the ethanol oxidation reaction (EOR) in such naturally chlorine-rich medium.

Methodology: The experiments based on voltammetry, electrochemical impedance spectroscopy, and galvanostatic and galvanodynamic assays were carried out following procedures previously described in the Group's previous works. In all cases, a single-compartment electrolytic cell using a three-electrode configuration was employed. A flat polycrystalline platinum electrode of 5x5 mm was set as the working electrode, while a high-surface-area platinum spiral was adopted as the counter electrode, and a reversible hydrogen electrode (RHE, with double junction in the case of measurements conducted at pH > 2 and < 12) served as the reference electrode. All solutions were prepared using analytical-grade reagents in high-purity water (Milli-Q, 18.2 MΩ cm). The measurements were performed using a potentiostat/galvanostat (model PGSTAT302N) from Autolab®, equipped with the manufacturer's Nova® interface, which served for both system control and data preprocessing. Before each experiment, both platinum electrodes were briefly heated to incandescence with a butane/air flame and then inserted into the argon-purged system, with the temperature maintained at 25 °C using a thermostat bath. The electrochemically active area of the polycrystalline platinum electrode was determined before each experiment - for normalization purposes - by integrating the charge from the hydrogen desorption region in voltammograms obtained for a 0.5 M H2SO4 solution at 50 mV s-1 and between 0.05 V and 1.2 V. The ionic compositions of the solutions used in the experiments were primarily based on the values provided by the international standard ASTM D1141-98 for preparing artificial seawater, in which components present in concentrations < 1 mMol kg-1 were here disregarded for simplicity. In each set of measurements, the ionic strength of the anionic components was kept constant by adding appropriate amounts of HClO4 or NaClO4 to ensure better control over any observed trends. Finally, ethanol was chosen as the organic compound of focus due to its simpler structural properties compared to other aliphatic alcohols. Additionally, its concentration in the electrolyte solutions of interest was limited to 1 M due to the low solubility of magnesium and calcium hydroxides and (bi)carbonates present in the medium at higher concentrations.

Preliminary results: In the presented investigation, a series of experiments was conducted to explore the electrochemical behaviour of platinum electrodes in the presence of ethanol-containing solutions with varying pH levels - and with an ionic composition resembling that found in seawater environments. Initially, it was observed that the oxidation of ethanol in the presence of chloride ions, typically encountered in seawater, is fundamentally impractical without prior removal of chloride ions. However, as the pH of the solution becomes more alkaline, distinct changes in the electrochemical profiles become apparent. Between pH 10 and extending through pH 12, there is a notable intensification and splitting of the main peaks associated with the formation and reduction of platinum oxide. This phenomenon appears to diminish as the pH approaches 14. Similarly, the peak associated with hydrogen adsorption on platinum (110) also undergoes a slight splitting at pH 10, with a subsequent decrease as pH approaches 14. The exact reasons for these pH-dependent effects remain under investigation, with our main hypotheses suggesting a complex interplay between pH and the rates of underlying surface processes. Furthermore, in the solutions containing 1 M ethanol, a significant increase in current density was observed as the pH increased from 10 to 12. This indicated a relaxation of the inhibitory effect of chloride ions on the adsorption of organic molecules as the pH levels became more alkaline. Additionally, a phenomenon of peak splitting in the oxidation of ethanol on the electrode surface was observed at pH 12. This splitting suggests the accumulation of ethanol-derived species with shorter lifetimes, which diminish as the pH approaches 14. Moreover, since dynamic periodic instabilities could potentially be harnessed to reduce the theoretical energy consumption in electrochemical devices that oxidize organic compounds, Preliminary experiments in this regard were carried out in the standard system at pH 8 but did not reveal any indications of current windows where such desired potential oscillations could be observed. However, a comprehensive series of tests across a broad pH range indicated not only the appearance but also a reduction in the average period of oscillations and an increase in the number of oscillations as pH increased. This trend suggests an enhancement in the catalyst's reactivity for ethanol oxidation, facilitated by improved surface self-cleaning in response to adsorbed poisoning species.

Preliminary conclusions: The results obtained indicate the fundamental infeasibility of oxidizing ethanol under the natural conditions in which seawater is found in the environment unless it undergoes beforehand a thorough secondary process of removal of the chloride ion. However, there is still the possibility of harnessing the increasing in the medium’s pH to reduce the specific adsorption of the Cl- anions on the electrode surface - thereby allowing appreciable current density values to be attained from the alcohol oxidation at potentials lower than those who would be required for water or chloride oxidation reactions. This not only reopens but also expands the range of applications possible for the system of interest as an aid for atmospheric CO2 capture and mineralization efforts. For instance, the flow of alkalized seawater into the organic compound oxidation system could be provided by the catholyte of an electrolyzer feed with a saline solution directly extracted from the ocean or discharged by a desalination facility. Such an approach can increase both the amount of H2 generated per liter of solution used and reduce the long-term implementation costs of these processes through the commercialization of higher-value products obtained from the incomplete oxidation of ethanol.

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Abstract Title: Stainless Steel as Catalyst for Ethanol Oxidation Reaction

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Abstract: This work investigated the viability of utilizing an austenitic stainless steel as an electrochemical catalyst for ethanol oxidation reaction (EOR), specifically the AISI310, which is rich in Ni. The catalytic activity for ethanol oxidation was examined using cyclic voltammetry. The reaction displayed sensitivity to the presence of various cations in the solution, indicating the influence of the size and intercalation of the ions in the superficial film of the Ni-containing electrode. The study also explored potential oscillations through galvanostatic experiments, revealing similar patterns with differences in frequency and potential window depending on the type of cation present. A Preliminary proposed mechanism for these oscillations suggests that NiOOH species are consumed during ethanol oxidation, limiting their availability for continued reaction by decreasing active sites and subsequent converting to Ni(OH)2. In summary, this study demonstrated that stainless steel electrodes have potential for ethanol oxidation and exhibit interesting catalytic characteristics. Nevertheless, questions persist regarding the influence of cations, indicating the necessity for future investigations to achieve a more comprehensive understanding of the electrochemical system under study.

Keywords: stainless steel, ethanol oxidation, nickel oxyhydroxide, oscillations.

Introduction and Objectives: Small organic molecules, particularly ethanol, show promise potential as power source due to its high hydrogen density, non-toxicity, ease of handling, and sustainable sourcing from biomass. Additionally, the CO2 produced during ethanol oxidation is part of the natural carbon cycle, originating from previously absorbed plant CO2. Employing noble metals as catalysts is not economically feasible due to their scarcity and high cost. Finding