Energy Transition
RESEARCH & INNOVATION

SÃO PAULO, BRAZIL | NOVEMBER 7-9, 2023

Energy Transition Research & Innovation Conference

ETRI 2023

BOOK OF ABSTRACTS

Research Centre for
Greenhouse Gas Innovation

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São Paulo, November 7-9, 2023

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We gratefully acknowledge the support of the RCGI – Research Centre for Greenhouse Gas Innovation (23.1.8493.1.9), hosted by the University of São Paulo (USP) and sponsored by FAPESP – São Paulo Research Foundation (2020/15230-5) and Shell Brasil, as well as the strategic importance of the support given by ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) through the R&DI levy regulation.

DOI: 10.5281/zenodo.12744754

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Keywords: Electrocatalytic, scillatory regime, ethanol.

Introduction and Objectives: The electrocatalytic oxidation of small organic molecules is of general importance for energy-related issues such as the fuel cells and electrochemical reform. The characteristics that emerge along the catalytic oxidation of small organic molecules critically depend on the coverage and nature of absorbates. The common emergence of current and potential oscillations in these reactions is closely related to the reaction mechanism and implies the overall conversion, and thus on the performance of practical devices. In the present work we study the dynamics of electrochemical oxidation of ethanol under oscillatory regime using tin-modified platinum electrode.

Methodology: Experiments were performed in a classical three electrode cell, polycrystalline platinum flags were used as working electrodes (WE), a graphite stick was served as counter electrode, and a reversible hydrogen electrode (RHE) was used as reference electrode. The experimental part includes protocols to invest control the effect of surface coverage using chronoamperometry and cyclic voltammetry, as well as studies under oscillatory regime.

Preliminary results: The results show that the efficiency of ethanol electro-oxidation is preferred powered, on a less poisoned electrode surface, which is obtained through a self-cleaning process driven by the oscillatory electro-oxidation.

Preliminary conclusions: The oscillatory electro-oxidation reaction of ethanol with the ordered intermediates of platinum and tin considerably affects the oscillatory dynamics, compared to the reaction at an unmodified platinum electrode. Overall, the results show a substantial increase in catalytic activity on platinum and platinum tin surfaces for the electro-oxidation of ethanol. These results are rationalized in terms of reaction mechanisms.

Murilo Gomes de Oliveira
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Abstract Title: Study of Ethanol Electrooxidation in Oscillatory Regime for Gaining Mechanistic Insights.

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Abstract: Ethanol is a candidate molecule to be used as fuel in the so-called Direct Liquid Fuel

Cells – DLFC's, but due to his sluggish kinetics of electro-oxidation and demanding of noble metals catalysts the practical usage in large scale is yet restricted. The complete ethanol electro-oxidation reaction (EEOR) can produce 12 electrons, but parallel routes lead to the formation of other byproducts, mainly acetaldehyde and acetic acid, in which only 2 and 4 electrons are extracted in the process respectively, lowering the efficiency. Despite many years of studies, the EEOR mechanism still not fully comprehended, so to shed some light and gather more information about the reaction mechanism, we are combining experimental studies in oscillatory regime with computational simulations of microkinetic modelling. Understanding how the EEOR proceeds can help in the rational design of catalysts and optimization of conditions to be used in fuel cells. In the presentation will be shown how we can use the complex dynamics of oscillatory regime to gain insights about the mechanism of ethanol electro-oxidation along with microkinetic modelling.

Keywords: Ethanol; electro-oxidation; reaction mechanism; modelling.

Introduction and Objectives: Kinetic instabilities and non-linear dynamics are common phenomena in the electro-oxidation of many small organic molecules, including ethanol. By applying the right conditions, we can observe oscillations of current and potential that can show mechanistic information that otherwise could not be seen with conventional technics. In oscillatory regime, reactions can be sort of "decoupled", so we can have a better understanding of the interaction between different intermediate species adsorbed in the catalyst surface. The main goal of the experimental investigation is to gain insights about how ethanol electrooxidation reaction proceeds and use this in microkinetic modelling to validate a mechanistic proposal.

Methodology: The experiments were conducted in a conventional three electrodes glass cell, with both working (WE) and counter electrode (CE) made of polycrystalline platinum. The electrolyte consisted of a solution of 0.5 mol L-1 of H2SO4. All potentials were measured against a reversible hydrogen electrode (RHE) made of the same solution of the electrolyte. The cell was constantly purged with argon. A potenstiostat/galvanostat Autolab PGSTAT302N was used for measurements. The ethanol concentration was varied from 0.05 to 1.0 mol L-1, and cyclic voltammetry and chronopotentiometry were recorded for all concentrations.

Preliminary results: The frequency, amplitude, waveform, duration, and potential drift of the oscillations in galvanostatic mode are highly affected by ethanol's concentration. This could be related to the products selectivity. In lower concentrations the route that produces acetic acid is

dominant, and acetate can adsorb and block active sites. In higher concentrations the route that produces acetaldehyde is dominant and the oscillations last longer.

Preliminary conclusions: The information gained in the study of ethanol electrooxidation in oscillatory regime are being used in microkinetic modelling simulations and can help to validate the mechanistic proposal. The knowledge of how the reactions proceeds at a surface level can be used for rational catalysts design and improvement of Direct-Ethanol Fuel Cells efficiency.

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Abstract Title: Perspectives of BECCUS technologies in Brazilian sugarcane sector

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Abstract: This study analyses the implementation of Bioenergy with Carbon Capture and Storage (BECCS) systems in ethanol production plants. Brazil is the world's largest producer of sugarcane and, therefore, has a great potential for coupling biofuel production with carbon capture and storage. The 2022/23 harvest reached more than 610 million tons of cane, which illustrate the magnitude of the sector, producing 37 million tons of sugar and 28.4 billion of liters of ethanol. The sugar and ethanol production process results in the production of large amounts of waste such as sugarcane bagasse, filter cake and vinasse, besides a huge energy and carbon capture potential by the large quantities generated. Thus, by implementing the BECCS technologies, Brazil has enough conditions to contribute to reduce global carbon emissions and to occupy a top position worldwide. In the specific case of the sugar and ethanol sector, CO2 generation and capture take place from bagasse burning and fermentation processes. Although, with the use of vinasse and filter cake for biogas production, the CO2 resulting from biogas purification to produce biomethane or also electricity production through the burning of biogas can also be captured. To illustrate the importance of implementing BEECS in the sugar-energy sector, a case study was carried out considering a medium-sized mill, whose installed sugarcane mill capacity is 1.6 million tons per harvest. This sugarcane process produced 13.7 million liters of ethanol, which results in the generation of 47,624 tons of filter cake and 1.58 billion liters of vinasse and 444,492 tons of sugarcane bagasse. With these scenarios the technical potential for