Anais

XXIV Simpósio Brasileiro de

ELETROQUÍMICA & ELETROANALÍTICA

Sociedade Brasileira de Eletroquímica e Eletroanalítica
SBEE

UNISINOS
DESAFIE O AMANHÃ.

PPGAD
Programa de Pós-Graduação
em Ambiente e Desenvolvimento

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Anais do XXIV Simpósio Brasileiro de Eletroquímica e Eletroanalítica

1ª edição

EDITORA
UNIVATES

Lajeado/RS, 2024

UNIVATES

Universidade do Vale do Taquari - Univates
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Coordenação: Prof. Dr. Carlos Cândido da Silva Cyrne
Editoração: Marlon Alceu Cristófoli

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Fone: (51) 3714-7024 / Fone: (51) 3714-7000, R.: 5984
editora@univates.br / http://www.univates.br/editora

S612 Simpósio Brasileiro de Eletroquímica e Eletroanalítica (24. : 2023 : Lajeado, RS)

Anais do XXIV Simpósio Brasileiro de Eletroquímica e Eletroanalítica, 2 a 5 de outubro de 2023, Lajeado, RS [recurso eletrônico] / Simone Stülp et al. (org.) – Lajeado : Editora Univates, 2023.

Disponível em: www.univates.br/editora-univates/publicacao/413
ISBN 978-85-8167-307-3

1. Eletroquímica. 2. Eletroanalítica. 3. Anais. I. Stülp, Simone. II. Rocha, Tatiane. III. Carvalho, Leandro Machado de. IV. Arsand, Daniel Ricardo. V. Dias, Daiane. VI. Hernandez Jr., Pedro. VII. Trombetta, Fernanda. VIII. Schneider, Alexandre. IX. Título.

CDU: 543.55

Catalogação na publicação (CIP) – Biblioteca Univates
Bibliotecária Gigliola Casagrande – CRB 10/2798

ISBN 978-85-8167-307-3

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ENABLING ETHANOL ELECTRO-OXIDATION IN SEAWATER-LIKE ELECTROLYTES THROUGH PH ADJUSTMENT

Resumo: The global temperature increase 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 CO_2 annually [1]. Among the existing mitigation alternatives, a promising one involves adapting the rapidly expanding desalination infrastructure worldwide for the parallel electrochemical capture and mineralization of CO_2 into chemically stable $CaCO_3$ and $MgCO_3$ salts - which can be safely stored in the seafloor for hundreds to thousands of years [2]. Many thermodynamic/technic constraints associated with the use of the of hydrogen oxidation (HOR, $E^\circ = 0V$ *vs* RHE) or oxygen evolution reactions (OER, $E^\circ = 1.23V$ *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 (<0.5V *vs* RHE) [3]. Nonetheless, the Cl^- anions in seawater (~0.56M) 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 [4]. 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 1M 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 $3mA.cm^{-2}$ at 0.69V (*vs* RHE) in a solution with a non-depleted chloride level of 0.5M 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.

Agradecimento: The authors would like to express their thankfulness for the financial support provided to this research by the all the funding agencies involved: FAPESP (#2019/22183-6, #2020/15230-5, and #2021/13002-8) and CNPq (#306060/2017-5).