Suppressing the Chlorine Evolution Reaction and Increasing Hydrogen Production During Seawater Electrolysis by Controlling Electrical Current Density

John W. Koster¹, Søren A. Tornøe², Donald C. Potts¹, Nobuhiko P. Kobayashi^{2*}

¹Ocean Science Department, University of California Santa Cruz, Santa Cruz, California, U. S. A.

² Nanostructured Energy Conversion Technology and Research (NECTAR), Electrical and Computer

Engineering Department, Baskin School of Engineering, University of California Santa Cruz, Santa

Cruz, California, U.S.A., *E-mail: nkobayas@ucsc.edu

Reducing the emission of greenhouse gases has given increased urgency to a long-standing quest for producing green hydrogen via electrolysis of water without generating harmful byproducts. In electrolysis of water, seawater offers substantial advantages over fresh-water: its higher electrical conductivity that reduces the overall electrical power required for electrolysis and its availability as a practically unlimited natural resource. However, the major obstacle for using seawater in electrolysis has always been the apparent kinetic advantage of chlorine over oxygen during electrochemical reactions at the anode, in other words, the Chlorine Evolving Reaction (CER) usually overwhelms the Oxygen Evolving Reaction (OER). As a result, toxic chlorine evolves at the anode. Conventional approaches for suppressing CER and promoting OER include the use of various catalytic coatings that promote OER, which frequently involves expensive chemical elements and complex chemical processes. Furthermore, the use of catalytic coatings often limits operational electrical current density J_c to 1 A cm⁻², which inevitably circumscribes the rate at which hydrogen is produced per unit time (i.e., hydrogen production rate) and is unavoidably reflected in the cost of resulting hydrogen. In this paper, we describe a new approach to suppressing CER and increasing the hydrogen production rate by using J_c larger than 10 A cm⁻² much larger than 1 A cm⁻² conventionally used in electrolysis. Fig. 1 shows the ionic conductivity of chlorine-the proxy concentration of chlorine species [C1]-plotted as a function of J_c , clearly demonstrating the suppression of CER by the use of higher J_c . As shown in Fig. 1, as J_c increased, [Cl] remains low ~0.06 µS in the range of J_c smaller than ~6 A cm⁻². [Cl] increases rapidly as J_c exceeds ~6 A cm⁻² to a maximum of ~0.52 µS at J_c ~9 A cm⁻², and then, [CI] declines

remains below 0.05 μ S for further increases in J_c . In addition to experimental demonstration, finite-element modeling indicates the drastic reduction in CER is associated with establishing a steep gradient in the electric field between a pair of electrodes via a significant reduction in the effective electrical conductivity of seawater. Our study suggests that explicitly elevating J_c to a level larger than 10 A cm⁻² creates opportunities for generating green hydrogen for use in large-scale and industrial applications by reducing CER negligible environmental to levels-an incentive-while increasing OER and hydrogen production rate-an economic incentive.

drastically to ~0.05 μ S at J_c ~12 A cm⁻², and subsequently, [Cl]



Fig. 1: Ionic conductivity of Cl-proxy concentration of chlorine species [Cl]-plotted as a function of J_c .