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In situ demonstration of anodic interface degradation during water electrolysis: Corrosion and passivation

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ABSTRACT

Understanding of interface-driven performance degradation in the oxygen evolution reaction (OER) is a prerequisite for developing long-term electrolytic systems operating at maximum efficiency. The question remains as to whether *in situ* observation of degradation during OER will be possible. We design a model system and fabricate a structure that is ideal for *in situ* detection of interfacial degradation that could occur at the anode, *i.e.* corrosion and passivation. The synthesized structure is based on carbon (C) or non-carbon (Ti); this is not only because it is a practical and general choice as an anode substrate, but also because it can represent the degradation reaction of corrosion or passivation, respectively. Interfacial responses from the ideally structured surface are observed (spectro)electrochemically under OER-operating conditions. We reveal that while electrochemical oxidation of C is inevitable over time, the passivation of Ti can be circumvented under controlled conditions. We also disclose that the use of Ti can be more beneficial for electrolytic cells, than that of C. These results highlight future research strategies required for the optimization of C- and Ti-based components used in electrolytic cells.

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1. Introduction

In the search for practical operation of electrolyzers and fuel cells, the designing and fabrication of effective system components used within them must be achieved. The generating unit, in which power or target chemicals are produced through electrocatalysis, consists of anode, cathode, and other supporting and auxiliary components [1–4]. As part of improving the efficiency of a generating unit, catalysts with increased number of active sites or enhanced intrinsic activity can be developed [1, 5–9]. At the same time, catalysts developed for prolonged catalytic activity must be thermodynamically stable within the electrolyte and electrochemically stable while functioning as electrocatalyst [10–12].

Three-electrode system testing in liquid electrolyte is an empirical method to examine the activity and stability of an electrocatalyst towards its target reaction. However, the excellent electrocatalytic performance of the half-cell does not always guarantee accordingly excellent performance in full-cell tests conducted using assembled cells made of solid electrolytes. Performance discrepancies

can be due to differences in configuration between them. When making assembled cells using a polymer electrolyte membrane, it is usually necessary to use additional components that are not essential for half-cells [1, 3, 4, 13, 14]. Examples are flow field plates (e.g. single-sided plates, bipolar plates), backing layers, and porous transport layers (e.g. gas diffusion layer) as shown in Supplementary data §1. The introduction of these components creates additional interfaces that can influence the electrochemical reactions that take place inside the cell.

Typically, the additional components are made of C- or Ti-based materials. This is because in general these materials can exist stably over a wide pH range and can be considered as electrical conductors [11, 12, 15, 16]. However, when anodic potential is applied, these materials also participate in electrochemical reactions, which can degrade the surface. Carbon can be corroded through carbon oxidation reactions (COR) in the potential regime required for the oxygen evolution reaction (OER). Corrosion is the degradation of the material and is a major cause of instability [17, 18]; therefore, the control of the degradation rate is at the heart of the electrochemical system for long-term operation [19–21]. In the case of Ti, a passivation layer can grow on top of it, thus reducing the electronic conductivity [11]. These parasitic reactions can degrade interfaces, so these reactions are a reasonable cause of interface-driven degradation.

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