An analysis of degradation phenomena in polymer electrolyte membrane water electrolysis

Christoph Rakousky [a], Uwe Reimer [a], Klaus Wippermann [a], Marcelo Carmo [a, *], Wiebke Lueke [a], Detlef Stolten [a, b]

[a] Forschungszentrum Jülich GmbH, IEK-3: Electrochemical Process Engineering, 52425 Jülich, Germany
[b] Chair for Fuel Cells, RWTH Aachen University, Germany

HIGHLIGHTS

- Durability of state-of-the-art PEM electrolysis tested for just over 1000 h.
- Reversible voltage increase recovers immediately after brief shut downs.
- Titanium contamination of electrodes and observed growth of Pt particles.
- Cell assembly highly affects results of CCM durability testing.
- Pt-coated PTL reduces degradation by 89%.

ARTICLE INFO

ABSTRACT

The durability of a polymer electrolyte membrane (PEM) water electrolysis single cell, assembled with regular porous transport layers (PTLs) is investigated for just over 1000 h. We observe a significant degradation rate of 194 $\mu V\ h^{-1}$ and conclude that 78% of the detectable degradation can be explained by an increase in ohmic resistance, arising from the anodic Ti-PTL. Analysis of the polarization curves also indicates a decrease in the anodic exchange current density, j_0, that results from the over-time contamination of the anode with Ti species. Furthermore, the average Pt-cathode particle size increases during the test, but we do not believe this phenomenon makes a significant contribution to increased cell voltages. To validate the anode Ti-PTL as a crucial source of increasing resistance, a second cell is assembled using Pt-coated Ti-PTLs. This yields a substantially reduced degradation rate of only 12 $\mu V\ h^{-1}$, indicating that a non-corroding anode PTL is vital for PEM electrolyzers. It is our hope that forthcoming tailored PTLs will not only contribute to fast progress on cost-efficient stacks, but also to its long-term application of PEM electrolyzers involved in industrial processes.

1. Introduction

'Green' electricity generated from renewable but intermittent sources (such as wind turbines and photovoltaics) can be stored in the form of hydrogen produced using polymer electrolyte membrane (PEM) water electrolyzers [1,2]. However, the widespread and cost-effective implementation of PEM water electrolysis as a means of storing electrical energy will only be possible when PEM electrolyzers can achieve lifetimes on the order of 50,000 to 100,000 h [3]. Unfortunately, to date the scientific community has

devoted very little attention to understanding the degradation mechanisms of cell and stack components. From the few studies of this topic that have been published, three main phenomena can be highlighted:

i) Passivation of Ti-based components on the anode side over time.
ii) Deactivation of electrolyte and electrode performance due to ion impurities in the feed water.
iii) Structural changes to the catalyst material.

With respect to i): Over time, high applied anode overpotentials facilitate the passivation of the Ti based components [4–7], leading

* Corresponding author.
  E-mail address: m.carmo@fz-juelich.de (M. Carmo).

to an increase in ohmic cell resistance and a subsequent increase of the cell voltage [4]. Pt-based and Au-based coatings are normally used to circumvent this passivation issue with bipolar plates [4,5,8,9]. However, the passivation of the Ti based porous transport layer (PTL) is only rarely taken into account [10–13] and the influence of a protective coating on performance degradation has yet to be fully quantified. Unfortunately, the protective coatings have a major impact on investment costs. In order to find new and cost efficient alternatives, the degradation mechanisms must be better understood and/or defined when using conventional Ti-PTL.

Regarding ii): Ion impurities present in the feed water (Fe, Cr, Cu, Na, etc.) were shown to accumulate in the catalyst-coated membrane (CCM), where they decrease the conductivity of the ionomer and electrode performance [14–20]. These effects relate to increased ohmic and charge transfer resistances [15] and were shown to be reversible when reactivating the CCM in sulfuric acid [14,15].

Finally, in the case of iii): As was shown ex situ, iridium active components can dissolve at high anode potentials, especially when the working electrode potential is varied [21,22]. However, at constant potential the effect of dissolution seems to be negligible [21]. During a long-term test, a reduction in the anode's catalyst area was associated with a decrease in the double layer capacitance and an increase in the charge transfer resistance [23]. Voltage cycling has also been shown to affect the cathode, where it facilitates the reduction of the electrochemically-active surface area (ECSA) of the platinum nanoparticles [24].

In this manuscript, durability profiles of single PEM electrolysis cells running under conventional operating conditions (80 °C, 2 A cm^{-2}) were obtained using both coated and uncoated commercial Ti-PTLs. Moreover, in order to relate the degradation mechanism to the Ti-PTL alone, all cell components and peripherals were protected against corrosion and the leaching out of metal ions, which would cause the membrane to critically degrade over time. Additionally, reproducible and efficient state-of-the-art commercial CCMs from Greenerity GmbH were used to reach meaningful conclusions.

2. Experimental

An electrolysis cell was operated at a constant current density of 2 A cm^{-2} for a period of about 1000 h (6 weeks), with an extension of 65 h, as can be seen in Fig. 1. Electrochemical and physical
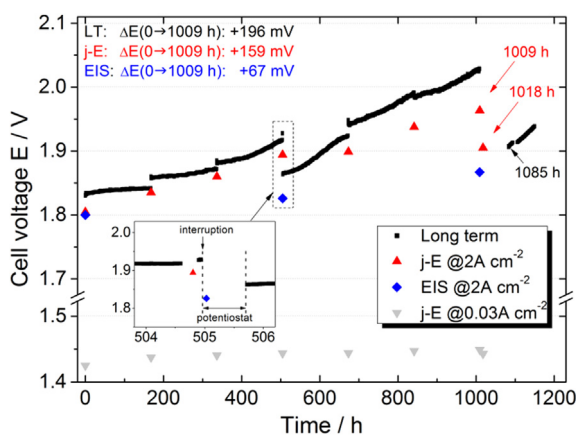

Fig. 1. Cell voltage at 80 °C during long-term operation at 2 A cm^{-2} (black squares). Triangles indicate the cell voltages during polarization curves (j–E) at 2 A cm^{-2} (upward) and 0.03 A cm^{-2} (downward). The times where EIS spectra were recorded and the cell voltages during the initial conditioning phase for the EIS measurements at 2 A cm^{-2} are marked with diamonds.

characterization methods were employed before, during and after the test in order to understand the long-term behavior of single cells and to locate the specific components undergoing degradation.

2.1. CCM and cell setup

The CCM samples tested were products by Greenerity GmbH. The anode catalyst layer contained IrO_2 and TiO_2 with an Ir-loading of 2.25 mg cm^{-2}. Pt/C was used as the cathode catalyst at a Pt loading of 0.8 mg cm^{-2}, while a Nafion® 117 membrane was used as the electrolyte. Two sheets of Toray paper (TGP-H 120) with a total thickness of 700 μm were used as the cathode PTL. Porous titanium sinter plates (GKN T3P, 42 × 42 × 1.3 mm) were used as anode PTL and will be referred to hereinafter as Ti-PTL. Platinum-coated titanium bipolar plates with serpentine-type flow fields were used on both sides, that on the cathodic side also being gold-plated. PTFE and silicone gaskets sealed the cell with an active area of 17.64 cm^2.

The half-cell potentials of the anodic and cathodic bipolar plates were recorded with respect to a dynamic hydrogen reference electrode (DHE) [25–28]. For this purpose, two platinum wires (0.1 mm diameter, Alfa Aesar) were hot pressed on the cathode side of the CCM using a strip of Nafion 212 membrane for fixing. The wires were placed in a parallel configuration (with a spacing of about 3 mm) in the catalyst-free area of the CCM, such that their tips were located about 3 mm from the edge of the catalyst-coated area. An electric current (DHE-current) of 12 μA was passed through the two wires to maintain constant hydrogen coverage of the negatively polarized Pt-wire, which was then used as the reference electrode. The voltage between the Pt wires (DHE-voltage) increased upon DHE start-up and reached a constant value after about 30 min. All half-cell potentials were then recorded after 60 min of continuous DHE operation. Due to instrument availability, no half-cell potentials are available before 210 h.

2.2. Test bench and long-term testing

Single cell experiments were performed using a test bench developed in-house. High purity feed water (18.2 MΩ cm) was circulated through both the anode and cathode compartments in separate water circuits at flow rates of 25 ml min^{-1}. Both water circuits were equipped with ion exchange resins to maintain a high degree of water purity. The cell temperature of 80 °C was reached by preheating the feed water to 75 °C and incorporating additional heating cartridges to stabilize cell temperature at all current densities. A DC power supply (TDK Lambda GEN-20-76) was used as the current source, while the cell voltages were read by a multimeter (Keithley Model 2701). A LabVIEW-based software was used to control all devices and record the data. In particular, the software ensures that no current drop occurs during a change of the operating current density, e.g., during polarization curves.

Before installation to the test bench, the cell was purged with deionized water at 80 °C for 4 h to remove potential ionic impurities. After installation to the test bench, the cell was kept hydrated at 80 °C until its dis-assembly at 1150 h. The long-term test at a current density of 2 A cm^{-2} lasted for a period of 1009 h. Before, during and after this period, electrochemical impedance spectroscopy (EIS) and polarization curves (j–E curves) were recorded. It should be noted that except for the times where EIS was recorded, the cell was never operated at cell voltages of less than 1.42 V which corresponds to the lowest voltage that was observed of the polarization curve. After 1009 h, the cell current was stopped and an additional polarization curve was recorded at 1018 h. During an extension period between 1085 h and 1150 h the current density was again set to 2 A cm^{-2}.