Nano Energy ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Fuel cell catalyst degradation: Identical location electron microscopy and related methods

Matthias Arenz [a,b,*], Alessandro Zana [a]

[a] Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark
[b] Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

ARTICLE INFO

Article history:
Received 22 December 2015
Received in revised form
14 April 2016
Accepted 16 April 2016

Keywords:
Pt
Proton exchange membrane fuel cells
Degradation
IL-TEM
IL-SEM
Ex-situ investigations

ABSTRACT

Fuel cells are an important piece in our quest for a sustainable energy supply. Although there are several different types of fuel cells, the by far most popular is the proton exchange membrane fuel cell (PEMFC). Among its many favorable properties are a short start up time and a high power density; both essential for automotive applications. Its drawback is the use of carbon supported Pt or Pt alloys as the active catalyst. The scarce resources of Pt led to significant efforts in reducing the amount of Pt used in PEMFCs. Thanks to the advancements of these efforts, catalyst stability gained increasing focus. Activity of the catalyst is important, but stability is essential. In the presented perspective paper, we review recent efforts to investigate fuel cell catalysts *ex-situ* in electrochemical half-cell measurements. Due to the amount of different studies, this review has no intention to give a complete overview and cover all studies. Instead we concentrate on efforts of our and other research groups to apply identical location electron microscopy and related methods to study the degradation of PEMFC catalysts.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

A sustainable (renewable), cost efficient supply of energy is one, if not the most important challenge for our future. Not only is the supply of affordable energy the driving force for many developments, sustainable energy supply will also help us facing the many environmental challenges that are related to the use of non-renewable energy. As most renewable energy sources, e.g. solar and wind energy, deliver transient, electric energy, the alignment of supply and demand is tightly related to sustainable energy. That is, in addition to develop the use solar and wind energy, we also need to provide solutions to convert, store and re-convert large amounts of electric energy. This is where electrolyzers and fuel cells come into play. They potentially offer the means of aligning our energy production to the demand with the help of energy carriers such as hydrogen.

It is beyond the scope of the this perspective review to discuss this framework; however, to provide viable solutions to above outlined challenge, fuel cells – the devices that convert the energy carrier back to electricity – need to be efficient and cost effective. For both properties the catalyst for the oxygen reduction reaction is essential. It needs to be highly active *and* to consist of reasonable abundant materials. Although Pt based catalysts most likely cannot provide long term solutions, today they offer the most promising pathway for commercialization of a range of fuel cells. This is largely due to the impressing advances that have been made in optimizing the activity of Pt, e.g. by alloying with a second metal [1–3]. With these advances the long term stability of industrial type high surface area carbon supported catalysts, here denoted as Pt/C or PtM/C, gained increasing attention. Activity and power targets are not the main concerns anymore, instead stability has become a paramount challenge [4].

There has been extensive literature published regarding the performance degradation of fuel cells and their catalysts [5–8]. Most of these studies have been conducted *in-situ*, i.e. in membrane electrode assemblies (MEAs) or fuel cell stacks, as their performance is the ultimate test for the use of consumers. In this perspective review, we limit ourselves to *ex-situ* methodologies, i.e. studies using electrochemical half-cells. *Ex-situ* studies cannot completely substitute *in-situ* investigations, but half-cell measurements provide a faster and cheaper way to scrutinize the stability of Pt/C based catalysts. Moreover a complete analysis of the degradation mechanism of fuel cell catalysts using *in-situ* techniques is not straightforward, whereas *ex-situ* studies allow a better control of the individual experimental parameters [9]. Nevertheless, *ex-situ* stability investigations are far less common used than *ex-situ* activity investigations [10] of catalysts and sometimes their scientific and predictive value is even questioned. This might be related to the fact that the majority of *ex-situ*

* Corresponding author at: Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland.
E-mail address: matthias.arenz@dcb.unibe.ch (M. Arenz).

http://dx.doi.org/10.1016/j.nanoen.2016.04.027
2211-2855/© 2016 Elsevier Ltd. All rights reserved.

Please cite this article as: M. Arenz, A. Zana, Fuel cell catalyst degradation: Identical location electron microscopy and related methods, Nano Energy (2016), http://dx.doi.org/10.1016/j.nanoen.2016.04.027

stability investigations of fuel cell catalysts simply report the loss in active surface area of the catalyst upon potential cycling. In view of this, in the recent years significant effort was put in the development of more sophisticated *ex-situ* stability investigation methodologies combining different characterization techniques. For example, half-cell measurements can easily be combined with differential electrochemical mass spectroscopy (DEMS) providing information about gaseous reaction products linked to the oxidation of the carbon support [11–15]. In this work, we concentrate on the combination of conventional half-cell measurements determining surface area loss with microscopic techniques developed to track morphological changes of the catalysts material at the nanoscale level, so called identical location electron microscopy.

2. Approaches for half-cell degradation studies

2.1. Experimental setup and protocols

In this section we will focus on the experimental protocols used to evaluate the durability of high surface area catalysts using *ex-situ* methodologies, i.e. measurements performed in electrochemical half-cells. Keeping in mind that *ex-situ* studies cannot completely replace *in-situ* investigations (i.e. studying MEAs and stacks), such studies provide i) a faster and cheaper way to screen the performance of catalysts and ii) a suitable tool for mechanistic studies of catalyst aging. By comparison a complete analysis of the degradation behavior using *in-situ* techniques is highly complex and the degradation is not necessarily an intrinsic property of the catalyst itself, but more of the catalyst layer. That is, in a fuel cell several parameters can influence the catalysts durability, such as relative humidity, partial pressures of the gases, temperature; but more importantly, also extrinsic factors as the quality of the MEA preparation itself. The same catalyst can perform quite differently in measurements applying the same degradation protocol depending on the MEA fabrication – which is in general proprietary knowledge. Furthermore *in-situ* degradation measurements last several days and up to several months [16].

In a conventional half-cell set up a three electrode configuration is adopted. A reference (RE), working (WE) and counter electrode (CE) are placed within the cell; they might be placed in three different compartments or in the same compartment. This configuration permits to probe the current potential relation at the WE with respect of the RE disregarding the interfacial potential difference of the CE. As in catalyst activity investigations, in *ex-situ* degradation studies the choice of right components is extremely important. The choice of RE and WE is relatively straightforward. Some of the most common RE electrodes are the Standard Calomel Electrode (SCE) and the Ag/AgCl electrode. These electrodes have the advantage of a high stability (measurements can take more than 12 h), but they might introduce contaminations into the system. In commercial *ex-situ* setups often all electrodes are simply placed into the same glass cell. However, even in double walled REs some ion exchange with the surrounding electrolyte might occur, thus poisoning the catalyst material. To avoid the diffusion of unwanted ions such as chlorides into the electrolyte, it is advisable to place the RE electrode in a separated compartment. In order minimize the iR drop between WE and RE while providing electrical contact and electrolyte exchange with the main compartment, in general a porous glass frit is placed at the bottom of the glass cell acting as Luggin capillary. An alternative separation method that completely avoids electrolyte exchange between the compartments can be achieved by using a Nafion membrane as barrier [17]. The WE in general consists of a Teflon tip with an embedded glassy carbon disk onto which the catalyst suspension is pipetted to form a catalyst film for the activity and/or macroscopic stability test [18–22].

The choice of the CE electrode and proper iR compensation are perhaps the most important aspect to consider. Most commonly a Pt mesh is used as CE in half-cell measurements. However, one needs to consider that the CE potential is free floating and the applied CE potential under fast cycling can change between very high and low values. Under these conditions severe Pt dissolution can take place and in the worst case Pt ions can redeposit onto the catalyst at the WE [23,24]. Therefore non Pt materials are preferred as CE in degradation tests. A good alternative is to use a glassy carbon rod with high surface area or if still Pt is the CE material of choice it should be placed in separated compartment in the same fashion as discussed before for the RE to confine the Pt ions [25].

Furthermore, one needs to careful check that the chosen potential window is indeed applied at the WE. Depending on potentiostat and software used, this may seem as being the case, but indeed is not. As often several thousand potential scans or potential steps are applied in a degradation tests, see below, and during fast potential cycling dissolution increases exponentially with the potential [26], small variations in the upper or lower potential limit can significantly influence the results. Deviations between the (by the software) selected and the applied potential window can occur for two reasons, the CE and improper iR compensation. If the CE area is too small, the applied potential might be limited by the potentiostat specification as large potentials/currents have to go through the CE. Often this is not seen in the recording software and can only be discovered by measuring the potential between RE and WE independent of the potentiostat software. Furthermore, if the iR drop is not properly compensated the measured and actual potential limits deviate. A good test is therefore to take a Pt WE and record a CV series between 0.05 and 1.2 V_{RHE} increasing the scan speed from 0.1 to 10 $V\,s^{-1}$. With proper iR compensation, normalizing the currents to the scan speed in the H_{upd} region of Pt the currents should exactly overlap, while the sluggish Pt oxidation leads to changes at higher potentials, see Fig. 1 [27].

Beside the experimental setup, the choice of potential treatment is essential. The accelerated stress test (AST) treatment must be designed to serve two purposes. First it has to provide a fundamental understanding of the physical and chemical degradation processes. Only a fundamental understanding of the different degradation mechanisms like Ostwald ripening, particle migration and coalescence, particle detachment and carbon corrosion will enable the design of considerably more durable catalysts than current standards. The second aim of an AST treatment should be to provide information about the degradation of the catalyst under realistic working conditions. A large variety of AST protocols have been presented in literature, consisting of potential holds, potential cycling with different scan rates, different temperatures, with or without rotation and different gas atmospheres. This variety of different AST treatments considerably limits comparability between different studies. Furthermore, only few AST treatments are designed by groups of experts with knowledge in both *in-situ* and *ex-situ* degradation studies. The aim of the AST treatment must be to simulate potentials and currents experienced by the catalyst in PEMFCs. At the same time the duration of the AST should be limited to avoid contamination effects. It is therefore important when choosing one AST over another, to carefully consider what the main purpose of the AST treatment should be [28,29]. That is for which application the PEMFC catalyst should be tested. Applying an AST protocol that simulates high potential cycling on a catalytic material that will be employed to work under constant potential conditions will not provide useful information on the degradation behavior of the catalyst being tested.

Please cite this article as: M. Arenz, A. Zana, Fuel cell catalyst degradation: Identical location electron microscopy and related methods, Nano Energy (2016), http://dx.doi.org/10.1016/j.nanoen.2016.04.027

Download English Version:

https://daneshyari.com/en/article/5452568

Download Persian Version:

https://daneshyari.com/article/5452568

Daneshyari.com