

## Review Article

# Toward developing accelerated stress tests for proton exchange membrane electrolyzers

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## Abstract

Proton exchange membrane water electrolysis is technically the most suitable technology for the production of green hydrogen on a large scale. Although it is still more expensive than hydrogen produced from fossil sources, it has already been commercialized. Novel components with cost-effective materials and efficient manufacturing processes are being rapidly developed. However, these components must endure durability tests that can guarantee a lifetime of at least 50,000 operation hours. Consequently, there is an urgent need to develop accelerated stress test protocols based on a deep understanding of degradation mechanisms of stack components. Recent reports show that the main degradation mechanisms are associated to anode catalyst dissolution, membrane chemical decomposition, and formation of semiconducting oxides on the metal components. These mechanisms can be accelerated by stressors such as high current density, dynamic operation, and shutdown modes. On the basis of these reports and knowledge of the operational requirements for large-scale proton exchange membrane water electrolysis, we propose an accelerated stress test protocol for the fast evaluation of newly developed cost efficient and durable components.

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## Keywords

Proton exchange membrane water electrolysis, Degradation, Accelerated stress test.

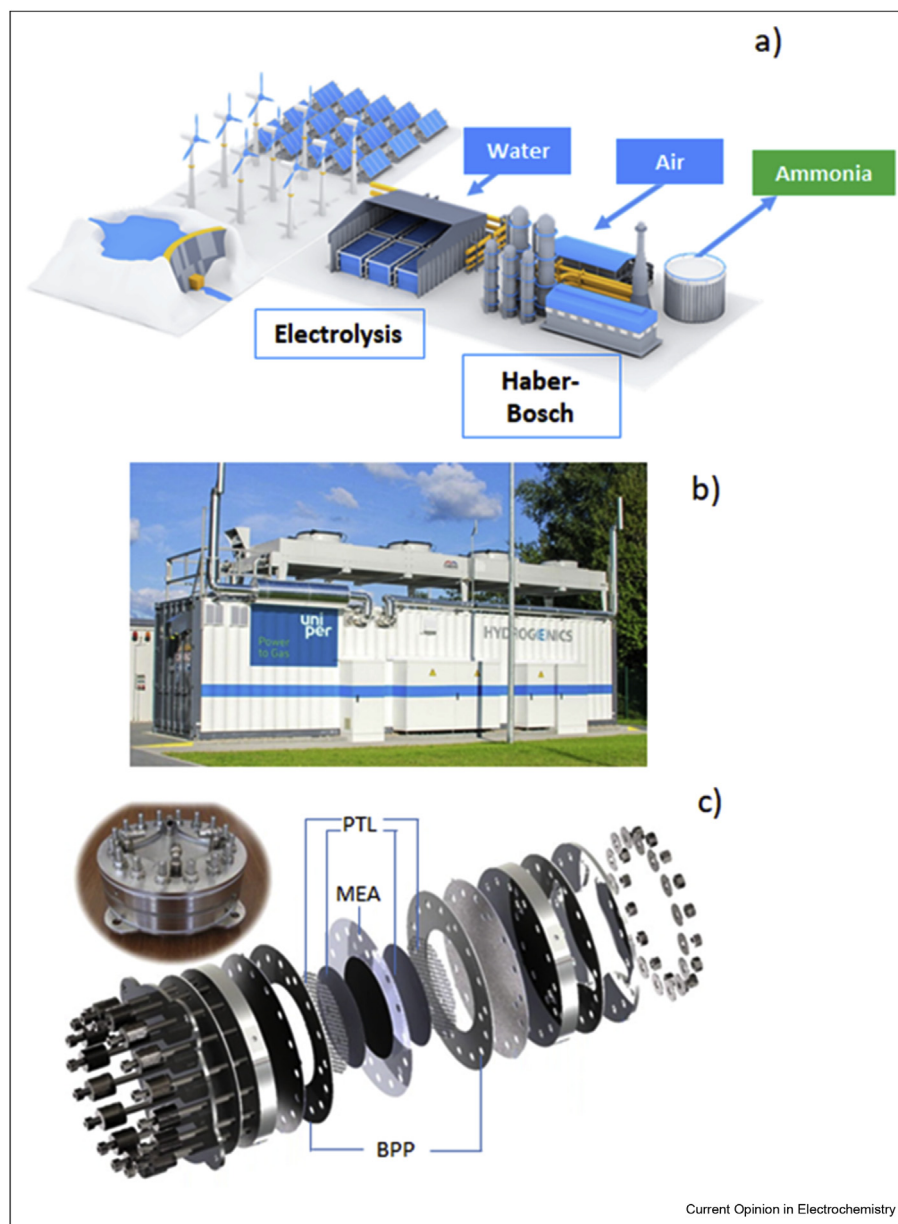
## Introduction

The chemical industry is a main consumer of hydrogen through refining and ammonia production [1]. More than 96% of the hydrogen produced worldwide currently comes from natural gas, oil, and coal resulting in an annual emission of 830 million tons of carbon dioxide into the atmosphere. This environment burden can be avoided by using ‘green hydrogen’ (i.e. carbon-neutral hydrogen) generated by water electrolyzer coupled to electricity from renewable energies. This topic is widely discussed within the European Commission, the US Department of Energy (DOE), and in industry [2–5]. In fact, there are various methods such as power-to-x (x = H<sub>2</sub>, methanol, ammonia) with the aim of energy storage by synthesis of valuable fuels. The concept of power-to-ammonia [6] is illustrated in [Figure 1a](#). The decarbonization of ammonia production industry requires gigawatt-scale electrolyzers. Alkaline water electrolysis (AWE) is already a mature technology, but because of its limited operating range and dynamics, it is impractical for the production of green ammonia. Proton exchange membrane water electrolysis (PEMWE), on the other hand, is very suitable for the application, but its dependence on expensive materials poses a serious risk for upscaling.

In 2014, the company Hydrogenics announced the construction of the first 1 MW PEMWE for power-to-gas plant [7] and started operation in 2014 ([Figure 1b](#)). In 2018, Shell started installing a 10 MW PEMWE from ITM Power in a refinery, covering only 1% of the plant hydrogen consumption [8]. Just one year later, Amprion and OGE announced the tender for a 100 MW electrolyzer for a power-to-gas project [9]. This unprecedented implementation of large-scale electrolyzers to produce green hydrogen could indeed lead to a significant reduction in CO<sub>2</sub> emissions. Nevertheless, the cost of green hydrogen is still up to three times higher compared with hydrogen produced by steam-methane-reforming [10]. This is largely because of the high cost of the PEMWE stack components [11].

The main components of a PEMWE cell are the membrane electrode assembly (MEA), porous transport layers (PTL), and bipolar plates (BPP) depicted in [Figure 1c](#). The anode of the MEA consists of iridium

Figure 1

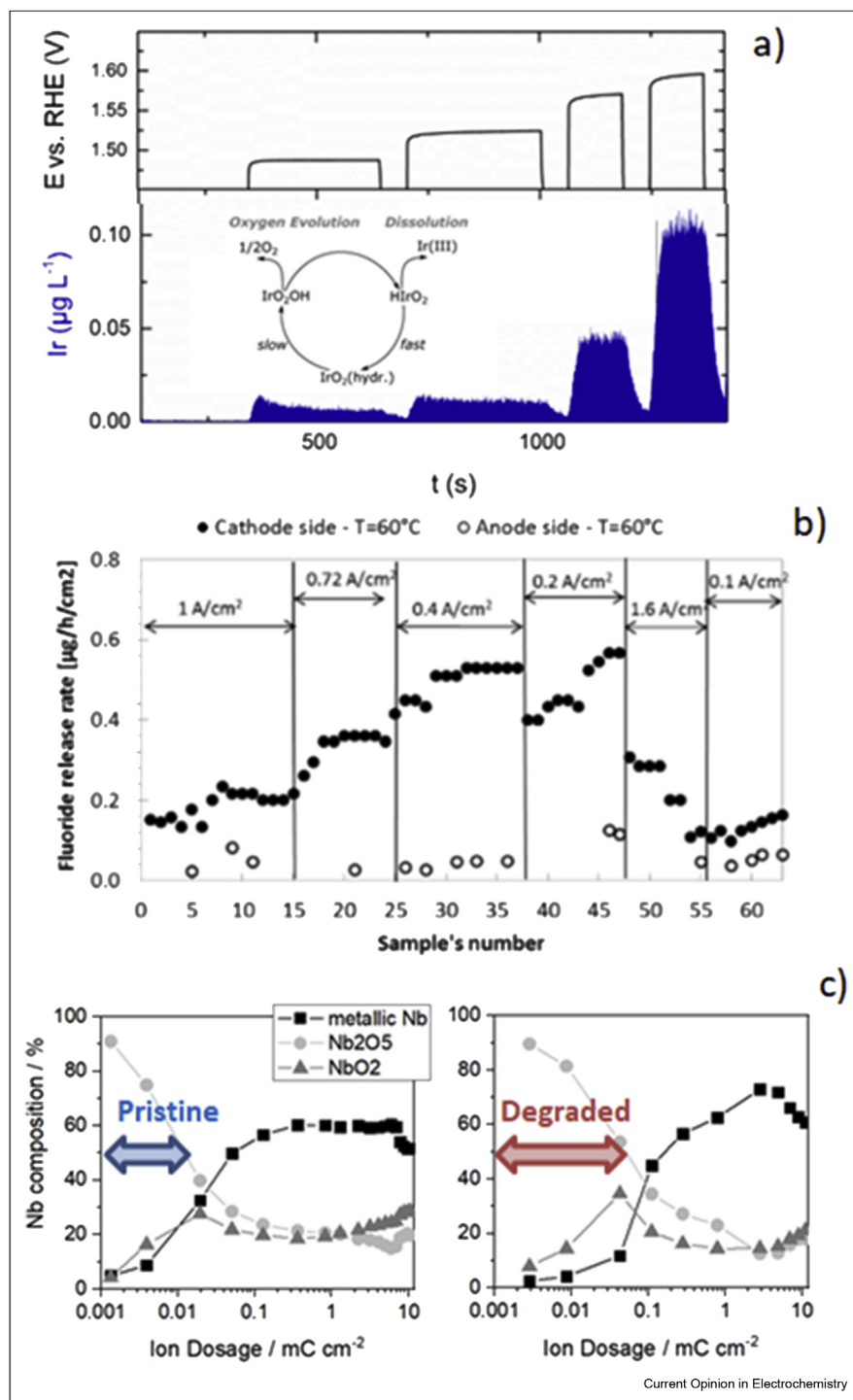


Applications of hydrogen in industry: (a) Power-to-Ammonia process using green hydrogen, with permission from ThyssenKrupp [6], (b) system in container reproduced from Ref. [7], and (c) PEMWE single cell components: MEA, Ti-PTL (sintered disc and mesh), and Ti-BPP, adapted from Selamat et al. [61].

oxide ( $\text{IrO}_x$ ) or in some cases a mixture of iridium and ruthenium oxides ( $\text{IrO}_x\text{-RuO}_x$ ). The cathode consists of Platinum (Pt) nanoparticles supported on carbon (Pt/C). The electrodes are separated by a polymer electrolyte membrane. The electrochemical splitting of water into  $\text{H}_2$  and  $\text{O}_2$  takes place in the catalyst layers. The task of the PTLs, which in most cases consist of Titanium (Ti) coated with precious metals, is to establish electrical and thermal contact and to ensure mass transport from or to the electrodes. The BPP has a similar composition to the PTL and acts as a separator

between different cells of a PEMWE stack and ensures mechanical stability [12,13]. Novel stack components are being developed by several groups and are showing promising results [14–17]. However, the commercial implementation of these innovations for large-scale electrolyzer is presently hindered by the lack of demonstration over the required operation time ( $>50,000$  h lifetime) [18]. Consequently, there is an urgent need to develop accelerated stress test (AST) protocols based on a deep understanding for degradation mechanisms. Moreover, it is also crucial to fully correlate

Figure 2



**Overview of relevant degradation mechanisms:** a) Dissolution rate of hydrous iridium oxide film in 0.1 M  $\text{HClO}_4$  in relation to the applied electrode potential steps (adapted from [62]). (b) Fluoride ion release rate with different current densities at  $60^\circ\text{C}$  from Ref. [36]; (c) XPS depth profile analysis showing the formation of Niobium-oxide ( $\text{Nb}_2\text{O}_5$ ) on aged Nb/Ti/ss BPP reproduced from Lettenmeier *et al.* [41].

and validate the AST results to those obtained through expensive and extenuating long-term runs. In this review, we discuss the most relevant contributions to the understanding of degradation mechanisms in

PEMWE as well as the conditions that accelerate aging. On the basis the most recent knowledge on these topics and the operation conditions defined by the users of the electrolyzer, we propose an AST that enables the

evaluation of newly developed stack components in a short period of time.

### Material/component degradation

The first step in developing AST protocols is to understand the degradation mechanisms of the different materials and components used in PEMWE. This topic has already been covered in several reviews [19–22]. Stack components such as catalysts, ionomers, membranes, PTLs, and BPPs undergo degradation, which depends strongly on the specific operating conditions. One particular issue is the irreversible degradation of the anode catalysts because of dissolution [23–25]. Figure 2a presents the dissolution rate of  $\text{IrO}_x$  during the oxygen evolution reaction (OER) in relation to the applied potential. The suggested mechanism is schematized in the inset of Figure 2a and shows the transition between  $\text{Ir}^{2+}$  (stable) and  $\text{Ir}^{3+}$  (unstable) complexes during OER. At the specified dissolution rates, the MEA would lose the entire anode catalyst in just a few hours in normal operation. Of course, this is not the case at all, which indicates that the dissolved  $\text{Ir}^{3+}$  is redepositing before it leaves the pores of the catalyst layer [26]. In addition, the stability and the associated degradation mechanism of various Ir catalysts can be significantly different. One example is the use of Ir–Ru oxides [27]. Ruthenium is available in some MEAs nominally marketed for electrolysis [28], but in many cases, the anode catalyst does not contain Ru because of its low stability [24,29,30]. Even Ir catalysts represent a mixture of elemental metal, metal oxides, and suboxides/hydrates. The stability of these are different and may or may not go through the same degradation mechanisms. One way to improve the stability of  $\text{IrO}_x$  catalyst against dissolution is to use antimony-doped tin oxide supports ( $\text{SnO}_2\text{:Sb}$ , ATO) [31–33]. The origin of the benefits of using the electroceramic support was recently revealed by operando near-ambient pressure X-ray photoelectron spectroscopy on PEMWE MEAs [34]. The  $\text{IrO}_x/\text{ATO}$  anodes show less formation of highly unstable  $\text{Ir}^{3+}$  species compared with unsupported  $\text{IrO}_x$  during OER in the PEMWE.

In addition to the anode catalyst degradation, the membrane and ionomer will also lose some of their properties over time under the different operation modes of a PEMWE. Membrane thinning can lead to increased gas cross-permeation effect and formation of hot spots, which will compromise the safety of the electrolyzer and cause fatal cell failure [35]. The ionomer degradation is evidenced by monitoring the fluoride release rate (FRR), which indicates membrane degradation [36]. The FRR increased in the PEMWE with rising temperatures and showed higher values at the cathode than at the anode, as seen in Figure 2b. Furthermore, the FRR decreases when the PEMWE is

operated with a high current density. Nevertheless, this dependence is not linear, and it is therefore difficult to associate a degradation mechanism to the phenomenon [37]. Further degradation of the membrane and catalyst layers is triggered by ionic contaminants ( $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$ ) in the feed water [38]. The cations occupy the ion exchange sites of the ionomer electrolyte in the catalyst layers and the membrane, resulting in increased anodic and cathodic overpotentials. Moreover,  $\text{Fe}^{3+}$  ions migrate from the anode to the cathode where they are reduced to  $\text{Fe}^{2+}$ , which leads to a loss of performance of the PEMWE [39]. The MEA contamination can be reversed by immersing the contaminated MEA in diluted  $\text{H}_2\text{SO}_4$  [38].

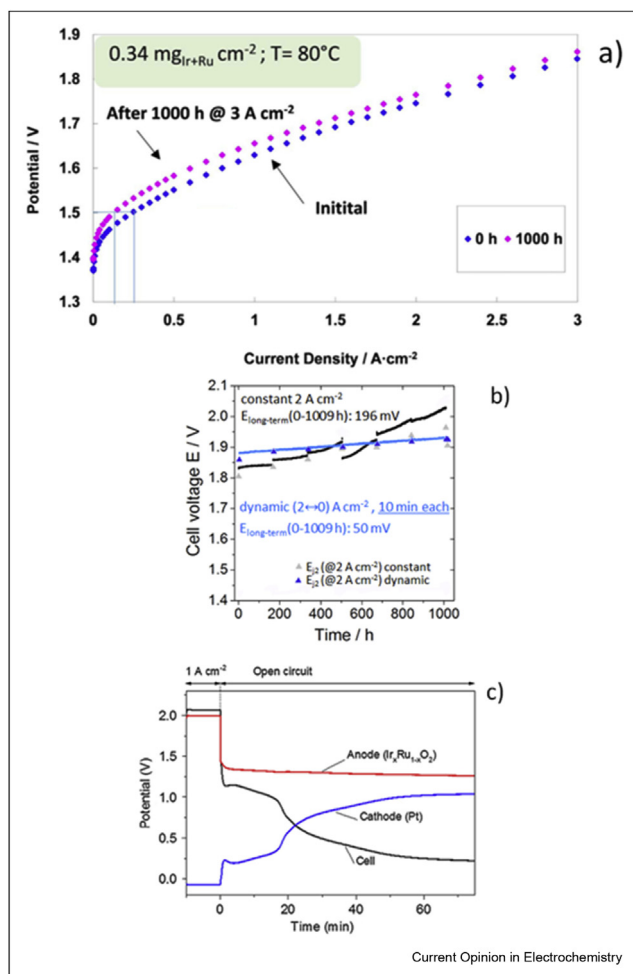
Another degradation mechanism is  $\text{TiO}_x$  formation on the Ti-PTL [12,37] and Ti-BPP [13,40]. This passivation process negatively affects performance because of increased contact resistance. This mechanism can be mitigated by applying protective coatings of Pt or Ir but it increases the component costs. However, the lack of plating on Ti components in many laboratory experiments skews the results, which are based on the oxide formation on the Ti surface. A more cost-effective solution to the Pt or Ir coatings, at least for the BPP, would be to use stainless steel instead of titanium and nonprecious metal coatings such as Nb/Ti [41]. Figure 2c shows the X-ray photoelectron spectroscopy depth profile analysis of an Nb-coated and Ti-coated stainless steel BPP, which was produced with magnetron sputtering physical vapor deposition and vacuum plasma spraying, respectively. Although  $\text{Nb}_2\text{O}_5$  is formed on Nb, this passivation layer is more conductive than  $\text{TiO}_x$  [41]. Furthermore, X-ray photoelectron spectroscopy depth profiles on BPP samples made of coated stainless steel showed after the test that the Nb coating prevented  $\text{TiO}_x$  formation beneath to Nb layer.

### Stressors

The second step in developing ASTs is to identify the stressors that accelerate the degradation effects discussed in the previous section. The high current density ( $>1 \text{ A cm}^{-2}$ ) mode of operation that increases the cell potential is probably the most dominant stressor that leads to irreversible degradation [42–45]. Reversible mechanisms have also been observed, although they have been poorly understood so far [46]. Figure 3a shows the polarization curves of a PEMWE with an Ir–Ru oxide catalyst as anode before and after 1000 h test at constant  $3 \text{ A cm}^{-2}$ . The degradation rate under this condition was three times higher compared to a test with a current density of  $1 \text{ A cm}^{-2}$  [47]. Measurements did not reveal any relevant evidence of an electrochemical surface area loss. According to electrochemical impedance spectroscopy, however, a slight increase of Coulomb charge was observed for the anode adsorption processes. The change of the slope of polarization curve



Figure 3



Stressor in cell performance and lifetime: (a) high-current density: electrolysis polarization curves for the low catalyst loading MEA before and after operation at 3 A cm<sup>-2</sup> for 1000 h at 80 °C with permission of [47]; (b) Dynamic operation: long-term development of the cell voltage in alternating operation at 2 and 0 A cm<sup>-2</sup> for 10 min each [37,53] (modified from references); (c) Shutdown: evolution of electrode potentials over time when switching from 1 A cm<sup>-2</sup> to open circuit shut-down from Ref. [54].

after 1000 h of operation was previously reported by Lettenmeier *et al.* [48]. This effect can be explained by a decrease of the Ohmic resistance of the cell when operating at high current densities. Post-test analysis using atomic force microscopy demonstrated an increased electronic surface conductivity of the anode catalyst layer because of loss of ionomer. This observation can explain the Ohmic drop over time and thus the change in the slope of the polarization curve.

The other two main stressors in PEMWE are the dynamic operating and shutdown process. These conditions are particularly relevant for electrolyzers used for grid services [37] or for the production of green hydrogen from fluctuating electricity from renewable energy such as wind or solar [49–52].

Studies show a loss of performance in cyclic operation mode with a low loading iridium catalyst [45]. Figure 3b shows the temporal evolution of the cell potential of two PEMWE operating at constant 2 A cm<sup>-2</sup> and under load cycling from 0 to 2 A cm<sup>-2</sup>. Partial recovery of  $R_{\text{total}}$  (and subsequently of cell performance) can be observed at about 505 h of operation at constant 2 A cm<sup>-2</sup>. This effect is associated with variations in the electric resistance of the Ti-PTL caused by the dissolution of Ti on the surface of the Ti-PTL during changes in the electrode potential [37]. While the constant operation resulted in a higher degradation rate of 0.2 mV h<sup>-1</sup> ( $E_{\text{long-term}}/\text{total time of 1000 h}$ ) compared to dynamic mode with 0.05 mV h<sup>-1</sup>, the effects of the fluctuating current on the Pt/C cathode catalyst were quite severe. The performance loss at constant current density can be attributed to the formation of semiconducting TiO<sub>x</sub> on the anode Ti-PTL. This problem can be easily solved by applying a thin film coating of Pt [37] or Ir [12]. However, the dynamic operation leads to degradation of the Pt/C cathode catalyst [53]. Indeed, the open circuit voltage (OCV) is about 1.5 V when no load is applied to the PEMWE or when it is turned off [54], which almost corresponds to the anode potential (Figure 3c). The cathode potential raises drastically until the OCV is reached, which leads to corrosion of the carbon support of the Pt/C catalyst and to agglomeration of the Pt nanoparticles. This effect results in loss of electrochemical surface area of the catalyst. Therefore, the cathode side of the cell is subject to severe wear during dynamic operation and shutdown. There are also different types of Pt/C catalysts (including those used for PEM fuel cells) that may have different stabilities in the electrolyzer cell. Finally, stressors such as temperature, differential gas pressure, and water quality are out of the scope of this analysis, because these parameters are specified by the different manufacturers of electrolyzers.

### Accelerated stress test protocols

EU Projects such as Novel [14] or NEXPEL [15] have made several attempts to develop AST protocols that combine the stressors of high current density and dynamic load cycling. However, these protocols are not linked to real operation scenarios of industrial PEMWEs. Some lessons can be learned from the development of AST protocols from PEM fuel cells, which is a similar technology to PEMWE and have some common components [55,56]. However, it is very difficult to link the AST to real life durability because many stressors are involved, and coupling effects make it very challenging to distinguish between their impacts on material degradation. Therefore, diverse single mechanism AST protocols exist including load cycling, start/stop, and OCV [57]. However, combined ASTs that resemble 'real' operating conditions are still under development [58].

Testing procedures are required to guarantee the expected durability in commercial PEMWE systems. These protocols should include information on the performance, efficiency, and durability of the electrolyzer [59]. The EU project QualyGridS [16] defines a set of protocols for the assessment of electrolyzer systems under specific duty cycles related to grid balancing applications. The protocols include operating modes such as constant, dynamic, stand-by as well as hot and cold start. Other protocols were defined for a 6 MW PEMWE of the EU project H2future [17], including operation modes in partial load, full load, and overload. In this context, the commercial electrolyzer needs to respond fast and will operate at full load or even overload with intermittent stand-by periods. Therefore, the ASTs protocols for PEMWE should include:

- (i) Nominal current density: this is not an intentionally accelerated condition, yet it will induce certain degradation.
- (ii) High current density operation: the impact will be mostly on the ionomer in the anode catalyst layer

and membrane. It will also affect the Ti-PTL and Ti-BPP if these are not coated.

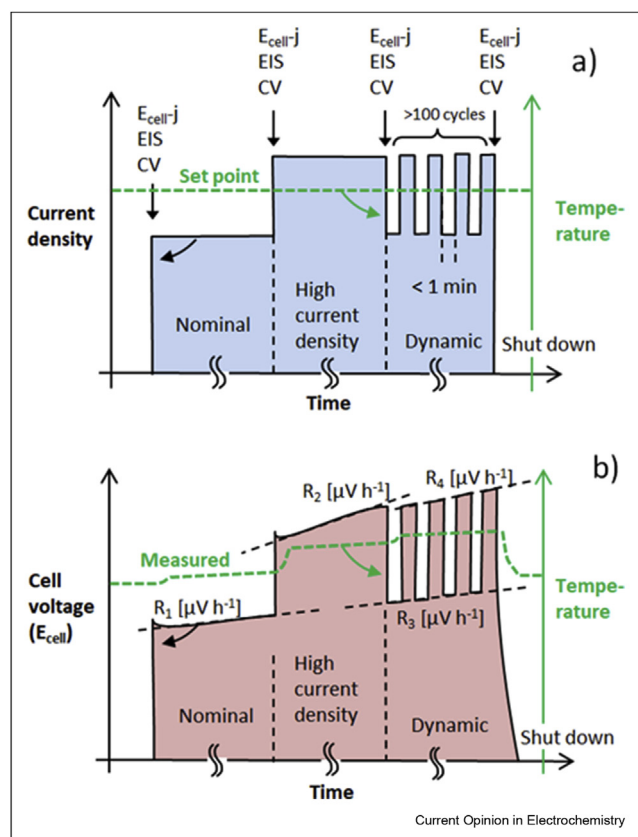
- (iii) Load cycling: it will cause degradation of the cathode catalyst.
- (iv) OCV or shut-down process: as for the load cycling profile, the main degradation effect will be on the cathode components.

The AST protocol considering all conditions is proposed in Figure 4; panel a) shows the load profile, while the voltage and temperature responses are provided in panel b). The stressors are applied in three subsequent periods at various current densities at a defined set-point temperature. At the beginning of test and with every phase change, we suggest applying potential–current curves ( $E_{\text{cell}}-j$ ), electrochemical impedance spectroscopy, and CV to monitor the state-of-health of the stack. The first period is nominal or full load. It is followed by the high current density or overload. The third period is the load cycling, which applies, for example, if the PEMWE is used to balance the electricity grid or to produce  $\text{H}_2$  from fluctuating renewable sources. Following this phase, a shutdown process of the PEMWE is initiated. All phases can be applied with variable timeframes, depending on which profile is relevant for the operating strategy of the PEMWE, for example, triggered by electricity cost or by surplus of renewables [60]. For each phase, there is a specific degradation rate ( $\mu\text{V h}^{-1}$ ) which can be used to estimate the lifetime of the electrolyzer. Thus, the proposed AST protocol herein is linked to the real-world applications of PEMWE and can be used to evaluate the stack components.

## Conclusions

The development of AST protocols for PEMWE will allow a time efficient evaluation of the durability of novel stack components. In this brief review, we have summarized the main degradation effects on the anode catalyst layer, the membrane and the Ti-based components, namely PTL and BPP. The dissolution of Ir is concomitant to the OER, whereas the membrane and ionomer release fluoride during the operation of the PEMWE. The Ti-PTL and Ti-BPL form semi-conducting oxide layers although these can be mitigated by using precious metal coatings. All of these degradation effects are expected to be enhanced with the applied current density. Furthermore, the carbon support of the Pt/C catalyst corrodes when the PEMWE operates dynamically and when it turns off. On the basis of reported degradation findings, we propose an AST protocol that includes the main operation stressors in PEMWE, that is, overload, dynamic operation as well as periods where no load is applied. The duration of each stressor phase period is defined by the specific scenario in which the PEMWE is to be used, such as grid

Figure 4



Proposed AST: (a) current density vs. time profile for accelerating degradation including all the main stressors PEMWE and the expected (b)  $E_{\text{cell}}$  profile with degradation rates (R). The goal of the proposed AST is to correlate the degradation rates  $R_1$  and  $R_3$  under nonstressing conditions with the degradation rates  $R_2$  and  $R_4$  under stressing conditions with high-current densities and dynamic operation.

balancing or power-to-chemicals. Finally, understanding the degradation mechanisms and conditions that accelerate aging is a vital part of developing ASTs. However, a unrepresentative PEMWE cell can result in misleading results and conclusions as well. Therefore, the establishment of a standardized PEMWE testing hardware is utmost necessary for the development of ASTs and evaluation of novel cell components.

## Conflict of interest statement

Nothing declared.

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- \* of special interest
- \*\* of outstanding interest

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