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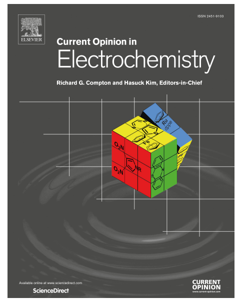

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The Challenges in Reliable Determination of Degradation Rates and Lifetime in Polymer Electrolyte Membrane Fuel Cells

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Key words

Polymer Electrolyte Membrane Fuel Cells; Reversible Degradation; Irreversible Degradation;

Recovery Procedure; Durability Evaluation

Abstract

The durability of polymer electrolyte membrane fuel cells (PEMFCs) needs to be further improved to cope with application requirements and economic competitiveness. This paper highlights the challenges in the reliable determination of degradation rates and lifetime. The reliable evaluation of performance degradation rates is fundamental to quantify and benchmark durability and to allow comparisons between PEMFC durability tests performed using different materials or in different laboratories. The use of efficient recovery procedures enables the discrimination of reversible and irreversible voltage losses and facilitates the understanding of recovery mechanisms. In the end, recent contributions about lifetime diagnoses and prediction are presented, which are promising to be implemented in PEMFC applications.

Introduction

As one of the most convenient and efficient devices to convert the chemical energy of hydrogen into electricity, polymer electrolyte membrane fuel cells (PEMFCs) have significant potential to reduce carbon dioxide emissions in modern society. To accelerate the commercialization of fuel cell technologies for transport applications, the European Commission set the 2030 technical goal of the lifetime of fuel cell systems for light duty and heavy duty vehicles as 7,000 h and 28,000 h, respectively[1]. Although significant progress is made in the development of fuel cell technologies within the last decades[2] and some applications are evaluated as ready for commercial deployment, e.g. fuel cell busses, high costs and limited longevity are still regarded as barriers to the large-scale production of fuel cells. In many expert assessments, the required fuel cell stack durability can be achieved in the near future while the promising commercial production is uncertain[3,4].

The lack of universal methods to deal with the remaining challenges with reliable determination of fuel cell degradation rates and lifetime directly leads to a large gap between a single cell in the lab and a stack in transport applications. This obstructs not only the improvement of fuel cell components and materials, but also the scale-up of fuel cells from the lab to the market. For example, many projects supported by DOE tracked the status of fuel cell durability by measuring the hours of operation before 10% of the beginning of life rated power was lost. But the cost was calculated based on the performance of a fuel cell system at the beginning of life and only partially considered the life of the stack or system[5].

Firstly, this work highlights several challenges of reliable evaluation of performance degradation rates, which is fundamental for the investigation of degradation mechanisms and for the provision of reliable input data for predictive models. In the second section, the impact of reversible and irreversible performance losses is emphasized, because the use of recovery procedures in durability tests can greatly affect the determined degradation rates. In the last section, several recent model-based performance diagnostic and lifetime prediction approaches are concluded. They provide promising tools to monitor the state of fuel cells online and to predict the lifetime in advance. Both aspects could greatly enhance the scale-up of fuel cells. Due to the complexity of fuel cells, the improvement of model-based performance evaluation approaches highly depends on a comprehensive understanding of degradation mechanism of fuel cells as well as on the reliable and comparable evaluation of fuel cell degradation rates using experimental data.

Reliable evaluation of degradation rates

Non-optimized operating conditions can seriously affect the performance and degradation of PEMFCs. Hence, it is important to determine critical operation parameters influencing performance[6,7,8]. Chen et al.[9] calculated the influential proportion (IP) of critical operating parameters on fuel cell performance with a three-dimensional model. From Figure 1 a), it is concluded that cell voltage is influenced mostly by cathode pressure and the cell temperature. Therefore, these parameters have to be controlled particularly precisely to reliably determine degradation rates. Besides, with the proposed experiment-based algorithm, Moein-Jahromi et al.[10] performed a set of parametric sensitivity studies of the impact of operating parameters on the Voltage Degradation Rate (VDR %) during durability tests in cyclic load protocols. Amongst the five considered parameters (temperature, relative humidity, pressure, minimum and maximum voltage of the load cycle), the most influential parameter on the VDR was the cell temperature. Similar investigations were performed to analyze the optimal operating parameters to minimize cell degradation during operation periods[11]. According to the data shown in Figure 1 b), the cell temperature, upper potential limit and the relative humidity are critical variables that affect performance losses[12]. Besides the studied operation conditions, the different IP of operating parameters in different models/works result from i) model input parameters, ii) model hypothesis and iii) governing equations.

Many in- and ex-situ characterization methods are used to evaluate performance degradation including polarization curves (IV), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), linear sweep voltammetry (LSV), etc[13,14]. Using these methods, the fuel cell performance degradation can be evaluated by changes in indicators like voltage and power during operation periods, low/high frequency resistance (LFR/HFR), electrochemical active surface area (ECSA), H_2 crossover, etc. Thereby, the changes of the indicators can also indicate reasons for the performance losses over operation time. Besides, the quantification of the contribution of each phenomenon to the degradation rate is important. However, it is the comparable and reliable evaluation of fuel cell performance degradation which is fundamental for this quantification and for the investigation of the performance degradation mechanisms.

The comparability and reliability regarding performance degradation measurements may vary using different test protocols, test hardware, and assumptions used for simulation. Jouin et al.[15] highlighted that in a durability test under constant currents, punctual characterizations with polarization curves and EIS disturbed the power and created transient stages. Consequently, the applied characterization methods and operational interruptions can impact the degradation behavior and have to be considered.

Furthermore, the evaluation of degradation rates of a fuel cell stack is always more challenging than in a single cell. The uniformity of performance distribution in a fuel cell stack was proved to reduce over time during a long-term test with constant current load[16]. As shown in Figure 1 c), in the PEMFC stack, three of the total thirty single cells showed a significantly higher performance degradation rate over time, while the mean cell voltage kept relatively stable. Thus, performance evaluation of single cells in a stack is necessary to avoid misinterpretations and malfunctions caused by reduced performance homogeneity.

In a review about fuel cell durability testing, the heterogeneous nature of the performance degradation in view of the stack hardware geometry was proposed and presented as Figure 1 d)[17]. The authors followed the degradation evaluations of commercial fuel cell systems and paid attention to the variation of the degradation rate versus the operation time. It was concluded that the rate of the cell voltage loss decreased over time. It can be emphasized that operation history is an important factor to reliably evaluate the degradation behavior.

Furthermore, Harms et al. [18] investigated specifically the variability and comparability of testing procedures for PEMFC stacks regarding performance evaluation. The results show that the fuel cell stack operated in a fuel cell system environment aged faster than in highly controlled test bench environment. Hence, it is crucial to determine critical operation parameters influencing performance for further adjustment and investigation of fuel cell behavior. For example, some groups optimized operating conditions by determining critical operation parameters [19, 20]. Suggestions about reliable determination of degradation rates is also reported before[21].

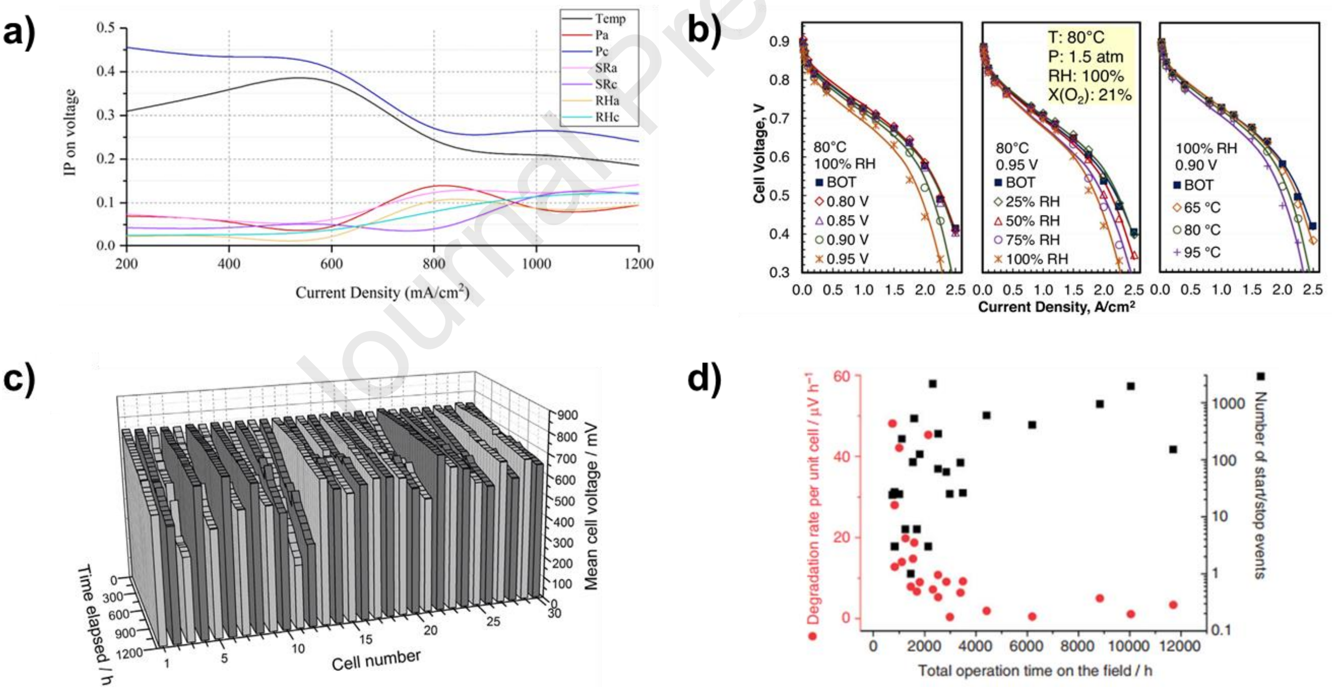


Figure 1 a) Effects of operating parameters on cell voltage. Influential proportion (IP) is quantitatively evaluated by equations[9].

b) Effect of exposure conditions (upper potential limit, relative humidity, cell temperature) on degradation of cell performance after 30,000 potential cycles[12]. The data as symbols are experimental while the solid lines are model results generated using equations with kinetic and transport parameters presented.

c) Distribution of voltage decay over time during a long-term test in a PEMFC stack consisting of 30 single cells[15].

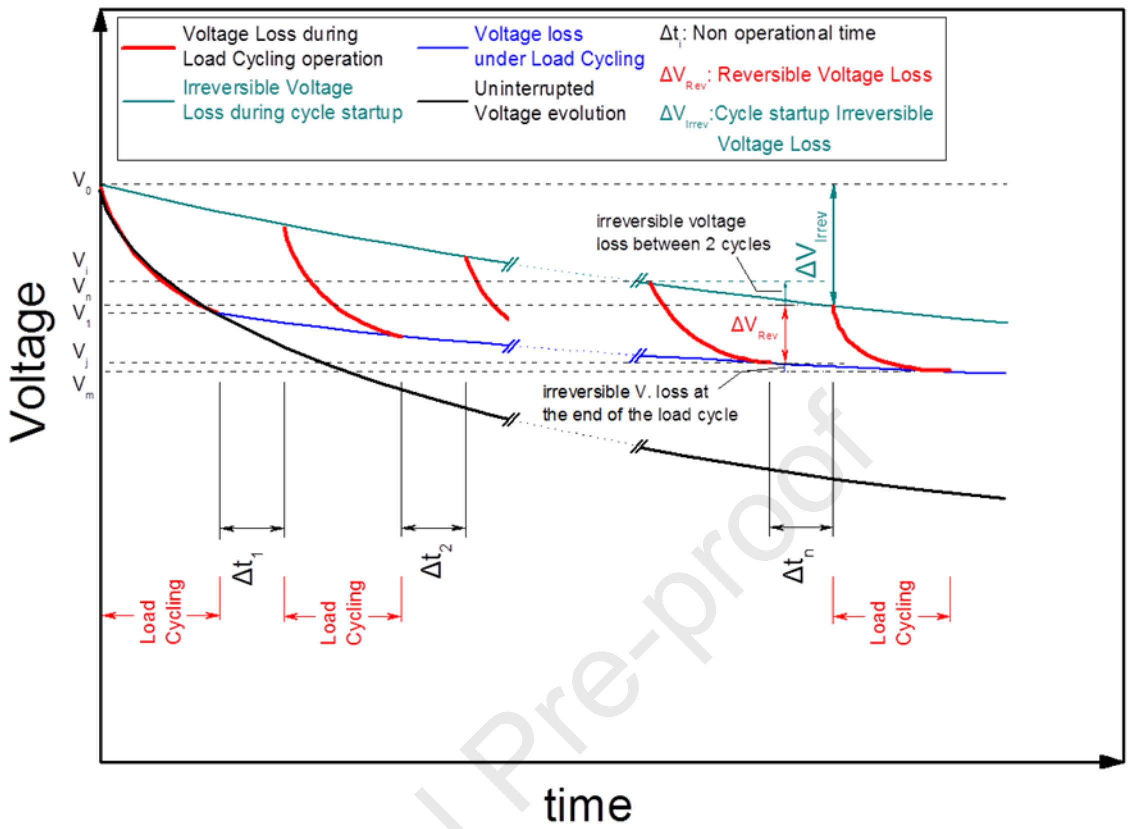
d) Variation of the degradation rate per unit cell versus the operation time on the field for commercial systems. The number of start/stop procedures undergone by the stacks is also given for information[14]. The nature of the MEA operated in these stacks is not identical and proprietary. In most cases, the systems were stopped before any failure.

Reversible/irreversible performance losses

Upon long-term operation the performance losses of PEMFC are found to be partially reversible and can be recovered by specific recovery procedures[22,23]. It was shown that effective recovery procedures can extend the lifetime of fuel cell systems since reversible and irreversible degradation processes are linked[24]. However, the comprehensive understanding of recovery mechanism is still under discussion. The Joint Research Center of the European Commission (JRC) provided a graphical description of reversible and irreversible contributions as shown in Figure 2 a)[25]. During PEMFC operation under specific load cycles, a recovery procedure is implemented after each operation period to recover the reversible performance losses. The reversible part of the voltage loss can be expressed as the difference between the cell voltage before and after the recovery procedure while the irreversible (non-recoverable) part of voltage loss is the difference between the cell voltage at the beginning or at the end of the previous and following operation periods[18]. Kundu et al. [26] reported that reversible performance degradation can also be extracted from the non-linear part of the voltage decay just after the recovery procedure and that this exponential contribution has a significant impact on the durability of the fuel cell. A simple method to describe the non-linear shape of the reversible voltage drop was proposed by Gazdzicki et al.[27,]. Besides, the irreversible performance contribution at a specific current density can be estimated from the linear part of the voltage decay at the corresponding current density[28].

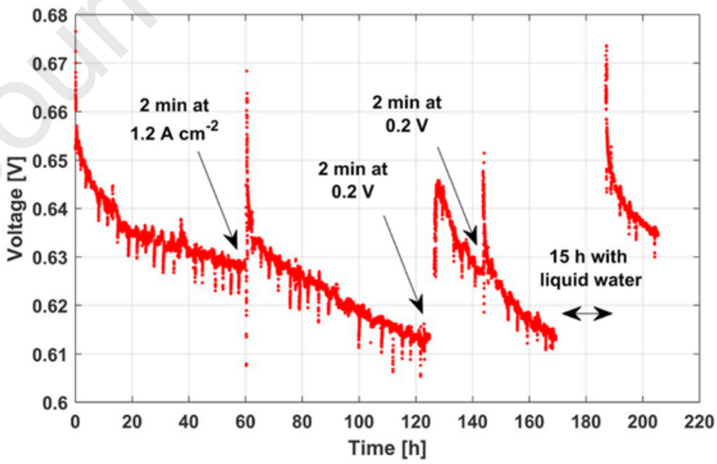
The general requirements for effective recovery strategies have been summarized in a review paper recently[23]. Specific recovery protocols are proposed by JRC[25] and United States Department of Energy (DOE)[29] which are recommended to be used to recover reversible losses periodically[25]. One of the technical targets of DOE is to propose a recovery procedure to recover over 95 % of the reversible performance losses in less than 30 s. Recently, two papers are published to provide a methodology to evaluate and to compare the effect of different recovery procedures in a durability test[30,31]. However, a uniform method to quantify the recovery effect of a specific recovery procedure is not established. Numerous papers addressed reversible degradation effects as well as the underlying degradation mechanisms[32,33]. Nevertheless, the development of reliable and efficient recovery procedures remains still a challenge and is needed to enable reliable performance and lifetime evaluation of fuel cells. In order to quantify the recoverable performance loss by a certain procedure, the cell is typically operated under a load profile which is systematically interrupted to recover the voltage decay. In the example shown in Figure 2 b)[34], the cell was operated at a constant current interrupted by different recovery procedures and for electrochemical characterization. It was concluded that the performance degradation due to the formation of Pt oxides on the surface of the cathode catalyst contributes partially to the reversible performance losses and can be recovered by exposure to an electrode potential of 0.2 V_{RHE}. Besides, the applied recovery procedure can help to understand the degradation mechanism of different materials used in fuel cells. To verify the two models about ionomer structural changes during low/high humidity operation proposed by Jomori et al.[35], Du et al.[36] compared the ECSA and oxygen transport resistance in pristine, aged and recovered membrane electrode assemblies (MEAs) with various ionomer/carbon ratios (I/C) as well as with and without Ketjen black carbon support (KB) surface modification (KB-mod and KB in Figure 2 c). For all the MEAs, the oxygen mass transport resistance increased significantly after operation and then was recovered to a large extent, while the ECSA kept almost constant. Thus, it is concluded that the dominating degradation mechanism of the MEA is the partial rearrangement of the ionomer in the catalyst layer, instead of the decreased ECSA. It is believed that the presence of liquid water is beneficial for the ionomer redistribution in the cathode CL. Thus, the ionomer movement is facilitated while creating micelles, which was also observed by some other groups before[37,38,39].

a)



Voltage Loss during Load Cycling operation
Voltage loss under Load Cycling
Δt_i: Non operational time
Irreversible Voltage Loss during cycle startup
Uninterrupted Voltage evolution
ΔV_Rev: Reversible Voltage Loss
ΔV_Irrev: Cycle startup Irreversible Voltage Loss
Voltage
time
irreversible voltage loss between 2 cycles
irreversible V. loss at the end of the load cycle
Load Cycling

b)



Voltage [V]
Time [h]
2 min at 1.2 A cm-2
2 min at 0.2 V
2 min at 0.2 V
15 h with liquid water

c)

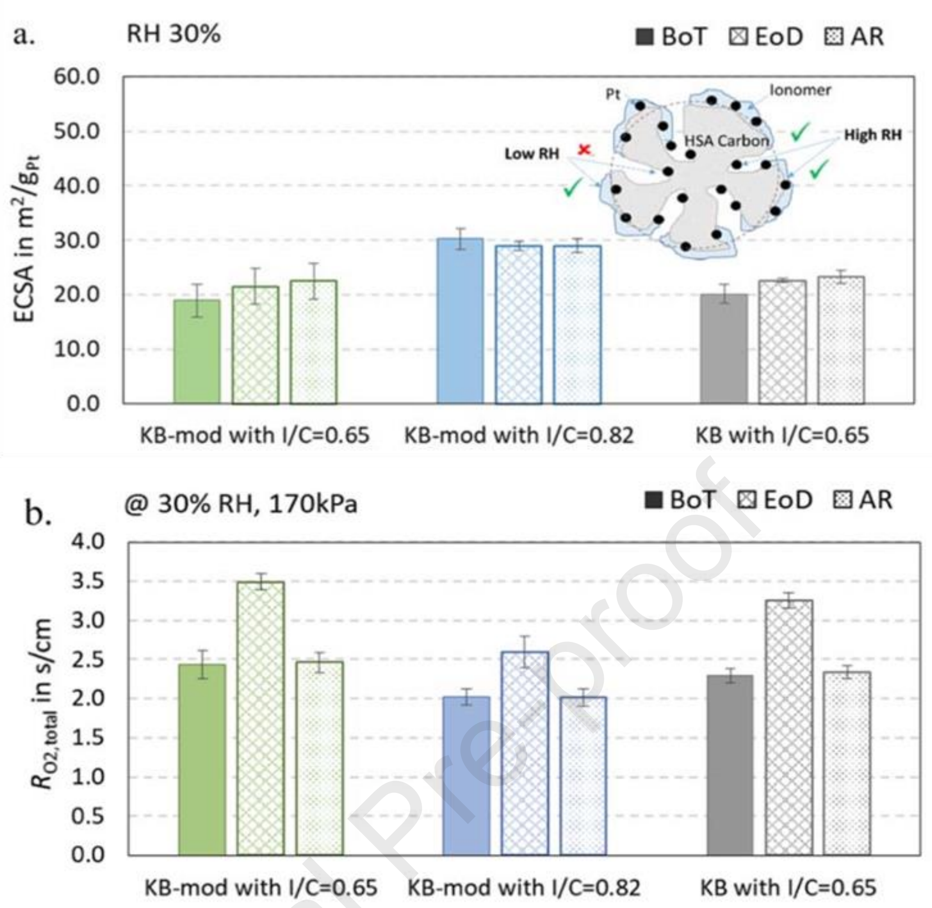


Figure 2 a) Graphical descriptions of reversible and irreversible performance degradation during a cell operation from JRC[25]. The figure was adapted from the reference.

b) Cell voltage of a commercial MEA during constant-current hold at 0.5 A·cm^{-2} interrupted by different recovery procedures[34].

c) Impact of recovery procedure on ECSA and O_2 transfer resistance. Values were measured at beginning-of-test (BoT), end-of-degradation (EoD, after aging tests) and after recovery step (AR) for different MEAs[36].

Performance diagnoses and lifetime prediction

For reliable and long-term stable operation of PEMFCs, status diagnoses, health monitoring and forecast methods for determination of remaining usable lifetime (RUL) have recently become of great interest[40]. For the performance diagnoses and monitoring, voltage and power are the commonly used health indicators since they are easy to measure and calculate. Nevertheless, information provided by these parameters is inevitably limited. Thus, other health indicators are proposed accordingly such as cell resistance, which also enables the analysis of failure mechanism[41]. Exemplarily, Husar et al. [42] proposed an experimental methodology including three indicators i.e. Tafel slope, mass transport resistance, and ohmic resistance. This method enables a simple and rough isolation of individual voltage losses which was determined by current interrupt and current sweep measurement. However, health indicators measured offline, such as due to the EIS and cycle voltammetry curves, cannot be used for on-line applications since additional equipment and time are required. Currently, researchers have made efforts to adapt these characterizations into the online performance diagnoses without upgrading the size of the fuel cell system. Depernet et al.[43] proposed the EIS performed by the power converter without additional hardware, cost and volume. Similarly, Lu et al.[44] designed a fast EIS measurement system through a current pulse injection circuit which enabled a feasible and effective EIS-based online fault diagnosis.

Various approaches are identified to forecast the RUL, such as based on data-driven[45] and model-based[46] approaches. While the data-driven approach has the disadvantage of deeply linking to the quality and quantity of the available data, the model-based method is the outcome of the comprehensive understanding of the fuel cell phenomena[47]. Thus, data-driven models are beneficial for the prediction of lifetime while the model-based models are beneficial for the extracting the health indicators of fuel cells. Till now, no universal complete prognostics tool is proposed for PEMFC systems, researchers mainly used data-driven or combined two approaches to reach a reliable and accurate RUL estimation[40]. Almost all the prognostic methods involve a learning phase and a prediction phase which exhibits a certain uncertainty. It is noteworthy that a successful learning phase is always based on the reliable evaluation of degradation rates. This enables the accurate and reliable lifetime prediction. As shown in Figure 3 a), during the learning phase, a degradation model is trained using parameter measurements from sensors in an operating PEMFC. Afterwards, the trained degradation model is used to estimate the system evolution until end-of-life conditions are reached[48]. Ahluwalia et al.[49] developed a model framework to project the performance degradation and to adapt operating conditions to minimize the cell degradation. Drive cycle simulations indicated that reducing the ratio of maximum to minimum inlet air flow rate and increasing cell temperature are needed to achieve the automotive technical target of 5000 h for MEAs with low loading of Pt group metals. To increase accuracy and facilitate decision making regarding RUL incremental models are used by Javed et al.[45], which means that training data are continuously updated when new data is available leading to updated and more accurate model parameters. The comparisons of the long-term prediction results with and without incremental learning are shown in Figure 3 b). Some novel approaches can also be applied to develop data-driven models for fuel cell degradation prediction, especially with the rapid development and application of the deep learning methodology in recent years[50]. Long short-term memory (LSTM) as a state-of-the-art artificial recurrent neural network (RNN) architecture has the advantage of classifying, processing and making predictions based on time series data[51]. Ma et al.[51] developed a grid LSTM (G-LSTM) model based on the paralleling and combining of individual LSTM cells. The proposed G-LSTM model was compared with LSTM model as shown in Figure 3 c). In the training phase, both models were successful in following most of the training data while in the predicting phase the error of G-LSTM model remained very stable.

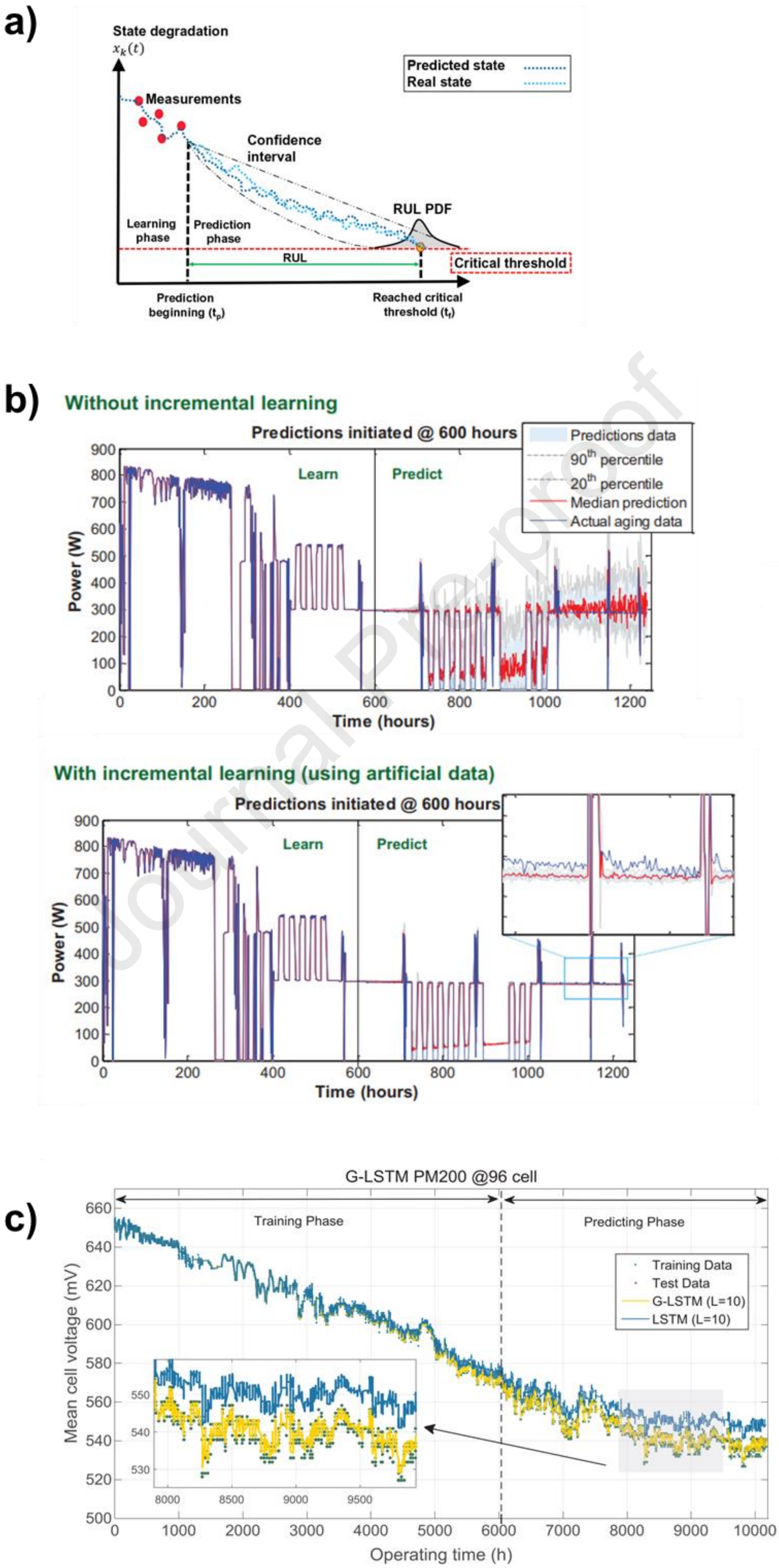

a)
State degradation
$x_k(t)$
Predicted state
Real state
Measurements
Confidence interval
RUL PDF
Learning phase
Prediction phase
RUL
Critical threshold
Prediction beginning (t_p)
Reached critical threshold (t_f)
b)
Without incremental learning
Predictions initiated @ 600 hours
Predictions data
90th percentile
20th percentile
Median prediction
Actual aging data
Learn
Predict
Power (W)
Time (hours)
With incremental learning (using artificial data)
Predictions initiated @ 600 hours
Learn
Predict
Power (W)
Time (hours)
c)
G-LSTM PM200 @96 cell
Training Phase
Predicting Phase
Training Data
Test Data
G-LSTM (L=10)
LSTM (L=10)
Mean cell voltage (mV)
Operating time (h)

Figure 3 a) Diagrammatic description of the entire prognostic process[48].

b) The long-term prediction results of PEMFC power with and without incremental learning[45]. Incremental learning: Prognostics models are re-trained and their parameters are updated according to new data available.

c) Predicting performance comparison between G-LSTM and LSTM approaches[51]. Long short-term memory (LSTM): An artificial recurrent neural network architecture used in the field of deep learning. The LSTM cell remembers values over arbitrary time intervals and regulates the flow of information into and out of the cell. Grid LSTM (G-LSTM) is a *two-dimensional architecture based on the paralleling and combining of individual LSTM cells.*

Conclusions

To enable reliable determination of degradation rates and lifetime, precise and reproducible methods to measure performance are required and the operating parameters have to be controlled carefully. In this context, cathode pressure and cell temperature are impacting performance most and, therefore, have to be controlled particularly precisely. Harmonized critical evaluation indicators of fuel cell performance during specific test protocols are supposed to be provided to enable data exchange and results comparison between different labs and fuel cells. The aspects such as fuel cell test bench environment, performance homogeneity, operation history and possible disturbance by characterization methods should be considered when evaluating the performance degradation.

A crucial aspect in determining degradation rate is to discriminate between reversible and irreversible degradation effects. However, a universal method to quantify reversible degradation and the recovery effect of a specific recovery procedure is not established. Moreover, punctual characterizations applied during a lifetime test can impact the degradation and recovery procedure itself and have to be considered when evaluating the degradation behavior. Besides, for performance degradation resulting from specific reasons, the recovery procedures should be designed appropriately to achieve the best recovery effect and avoid the application of non-optimized recovery procedures.

Eventually, based on the current understanding of fuel cell degradation mechanism and on the reliable analysis of experimental data in laboratories, prognostic methods can be developed to predict the remaining lifetime of a PEMFC. The applied methods typically consist of a learning phase and a prediction phase. However, it is still challenging to increase the accuracy of long-term prediction of the lifetime of PEMFC systems.

Conflict of interest statement

Nothing declared.

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Voltage Losses due to Ionomer Migration, Journal of the Electrochemical Society 167(14) (2020) 144513-144527.

After a prolonged degradation protocol under low RH, the performance decay can be recovered by a high RH recovery step. The reversible performance decay results from ionomer structural changes caused by the dry conditions. The ionomer displacement, induced by operations under low RH conditions and sequentially high RH, not only causes irreversible ECSA losses directly, but inevitably induces further irreversible losses when the fuel cell returns to its normal wet operational conditions.

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The objective of this study is to describe the methodology used to isolate the main voltage loss indicators through a simple and effective treatment of a current interrupt and current sweep. The voltage loss indicators are activation polarization, mass transport, and ohmic losses. The indicators for these losses are the Tafel slope, mass transport resistance and ohmic resistance, respectively. The use of this methodology to isolate the individual voltage losses works quite well.

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A model framework for projecting performance degradation is developed using data taken on differential cells. The operating conditions to minimize cell degradation on drive cycles are identified to achieve the required longevity of the PEMFC system.

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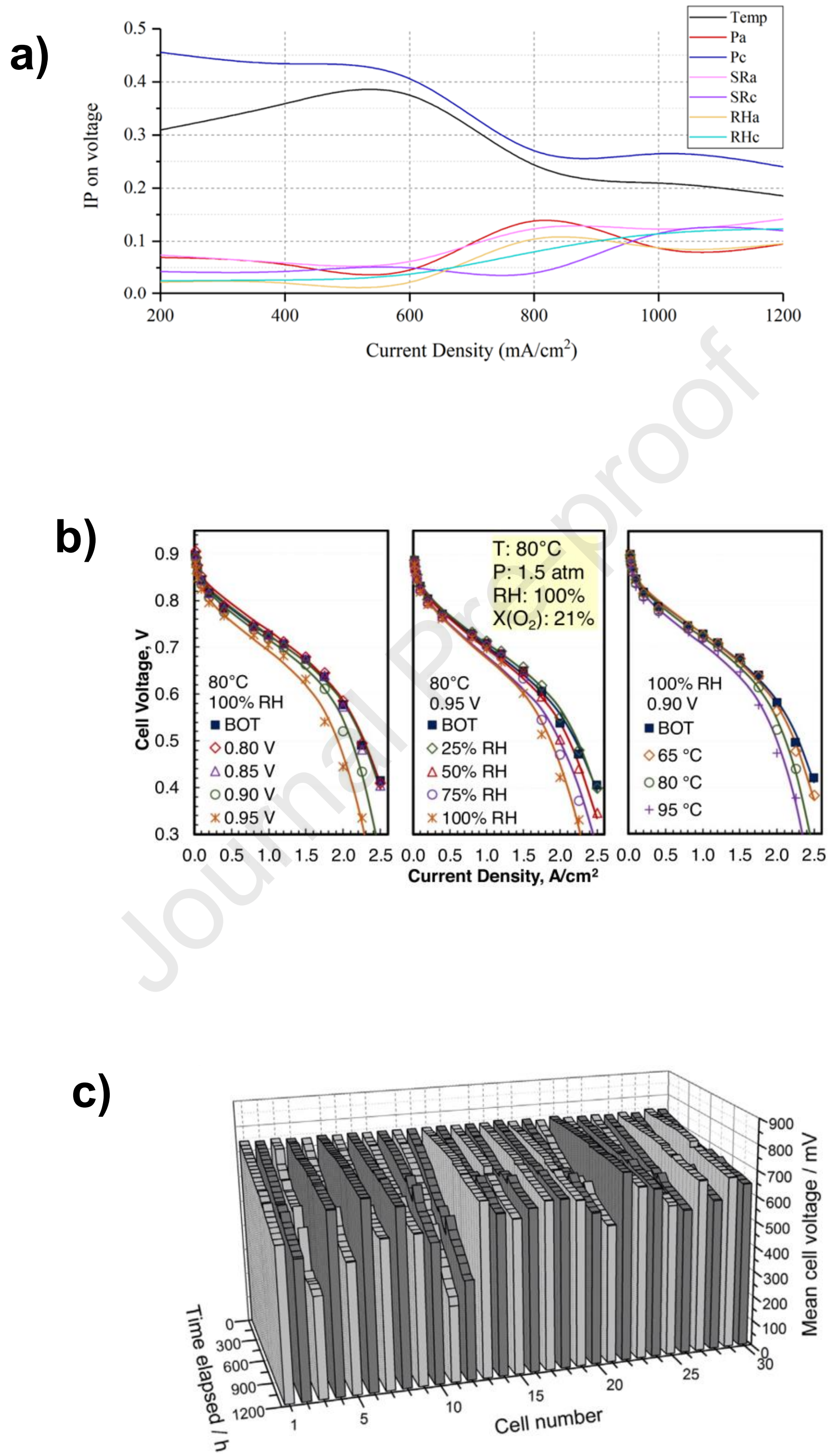
An innovative fuel cell degradation prediction method is proposed using Grid Long Short-Term Memory (G-LSTM) recurrent neutral network (RNN) which is suitable for long-term prediction of PEMFC performance. The proposed prediction model is experimentally validated by three different types of commercial PEMFC systems to increase the accuracy. The results indicate that the proposed model can efficiently predict the fuel cell degradation in a more precise way in comparison with the normal LSTM model.


a)
Temp
Pa
Pc
SRa
SRc
RHa
RHc
IP on voltage
Current Density (mA/cm²)
b)
T: 80°C
P: 1.5 atm
RH: 100%
X(O2): 21%
80°C
100% RH
BOT
0.80 V
0.85 V
0.90 V
0.95 V
80°C
0.95 V
BOT
25% RH
50% RH
75% RH
100% RH
100% RH
0.90 V
BOT
65 °C
80 °C
95 °C
Cell Voltage, V
Current Density, A/cm²
c)
Mean cell voltage / mV
Time elapsed / h
Cell number

d)

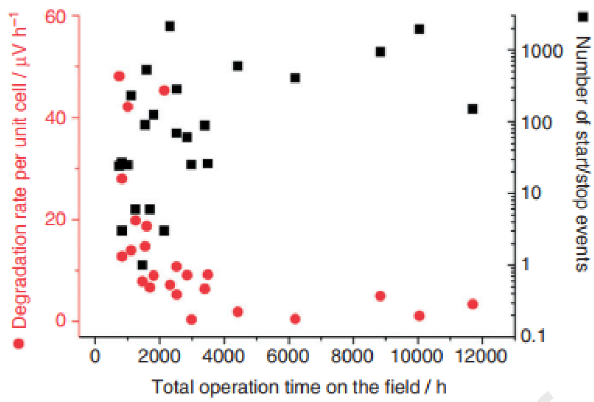


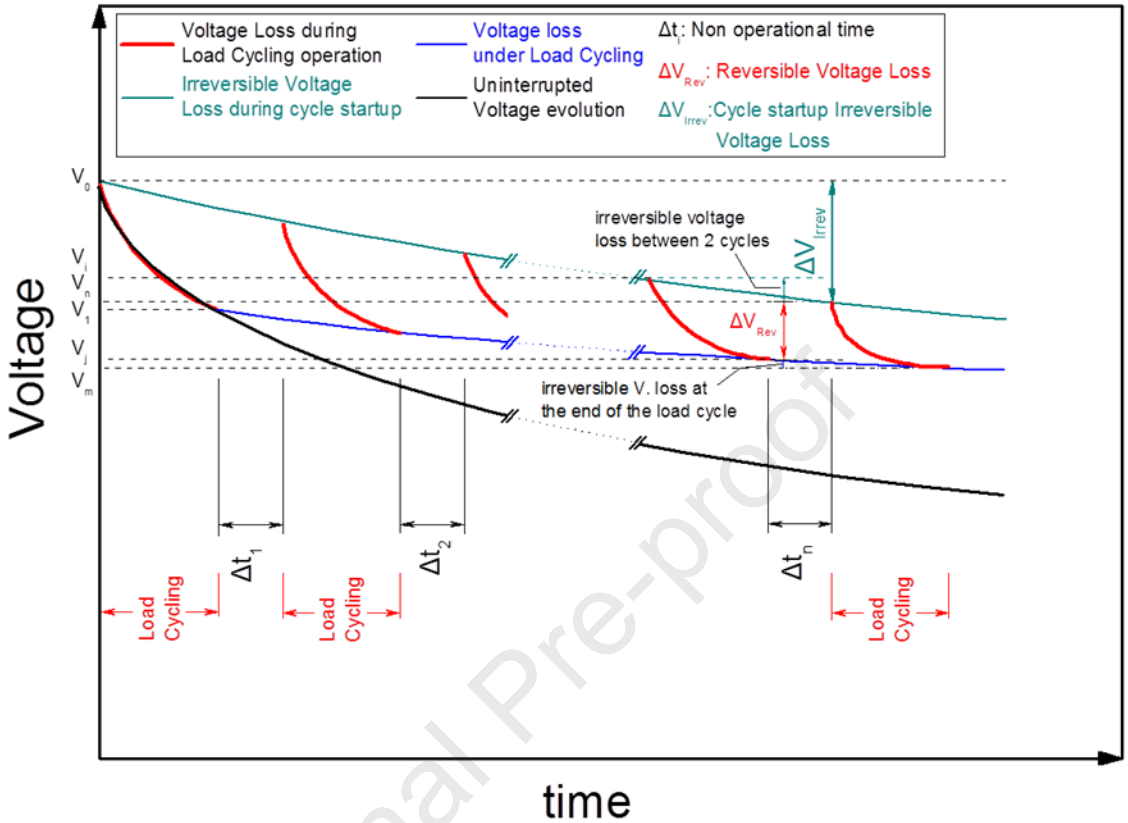
Figure 1 a) Effects of operating parameters on cell voltage. Influential proportion (IP) is quantitatively evaluated by equations[9].

b) Effect of exposure conditions (upper potential limit, relative humidity, cell temperature) on degradation of cell performance after 30,000 potential cycles[12]. The data as symbols are experimental while the solid lines are model results generated using equations with kinetic and transport parameters presented.

c) Distribution of voltage decay over time during a long-term test in a PEMFC stack consisting of 30 single cells[15].

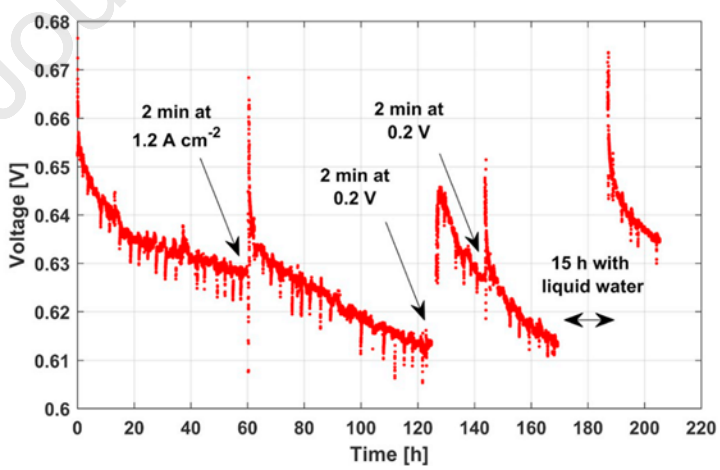
d) Variation of the degradation rate per unit cell versus the operation time on the field for commercial systems. The number of start/stop procedures undergone by the stacks is also given for information[14]. The nature of the MEA operated in these stacks is not identical and proprietary. In most cases, the systems were stopped before any failure.

a)



Voltage Loss during Load Cycling operation
Voltage loss under Load Cycling
Δt_i: Non operational time
ΔV_Rev: Reversible Voltage Loss
Irreversible Voltage Loss during cycle startup
Uninterrupted Voltage evolution
ΔV_Irrev: Cycle startup Irreversible Voltage Loss
V_0
V_i
V_n
V_1
V_j
V_m
irreversible voltage loss between 2 cycles
ΔV_Irrev
ΔV_Rev
irreversible V. loss at the end of the load cycle
Δt_1
Δt_2
Δt_n
Load Cycling
Load Cycling
Load Cycling
Voltage
time

b)



2 min at 1.2 A cm-2
2 min at 0.2 V
2 min at 0.2 V
15 h with liquid water
Voltage [V]
Time [h]
0.68
0.67
0.66
0.65
0.64
0.63
0.62
0.61
0.6
0
20
40
60
80
100
120
140
160
180
200
220

c)

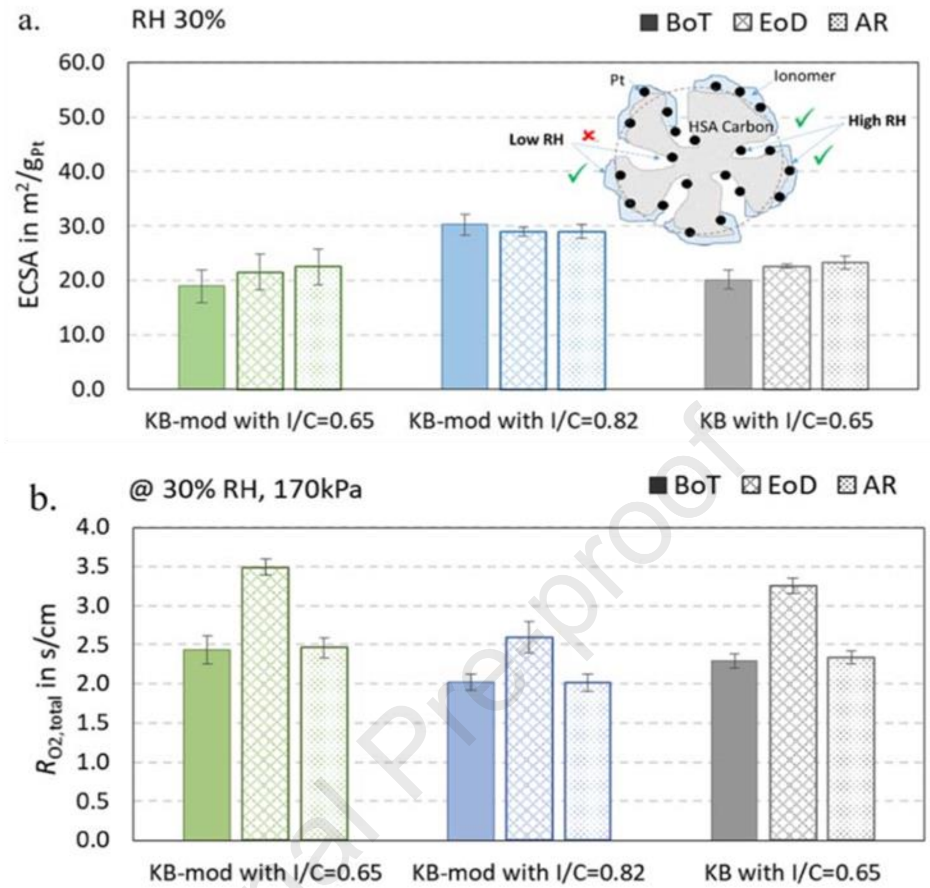
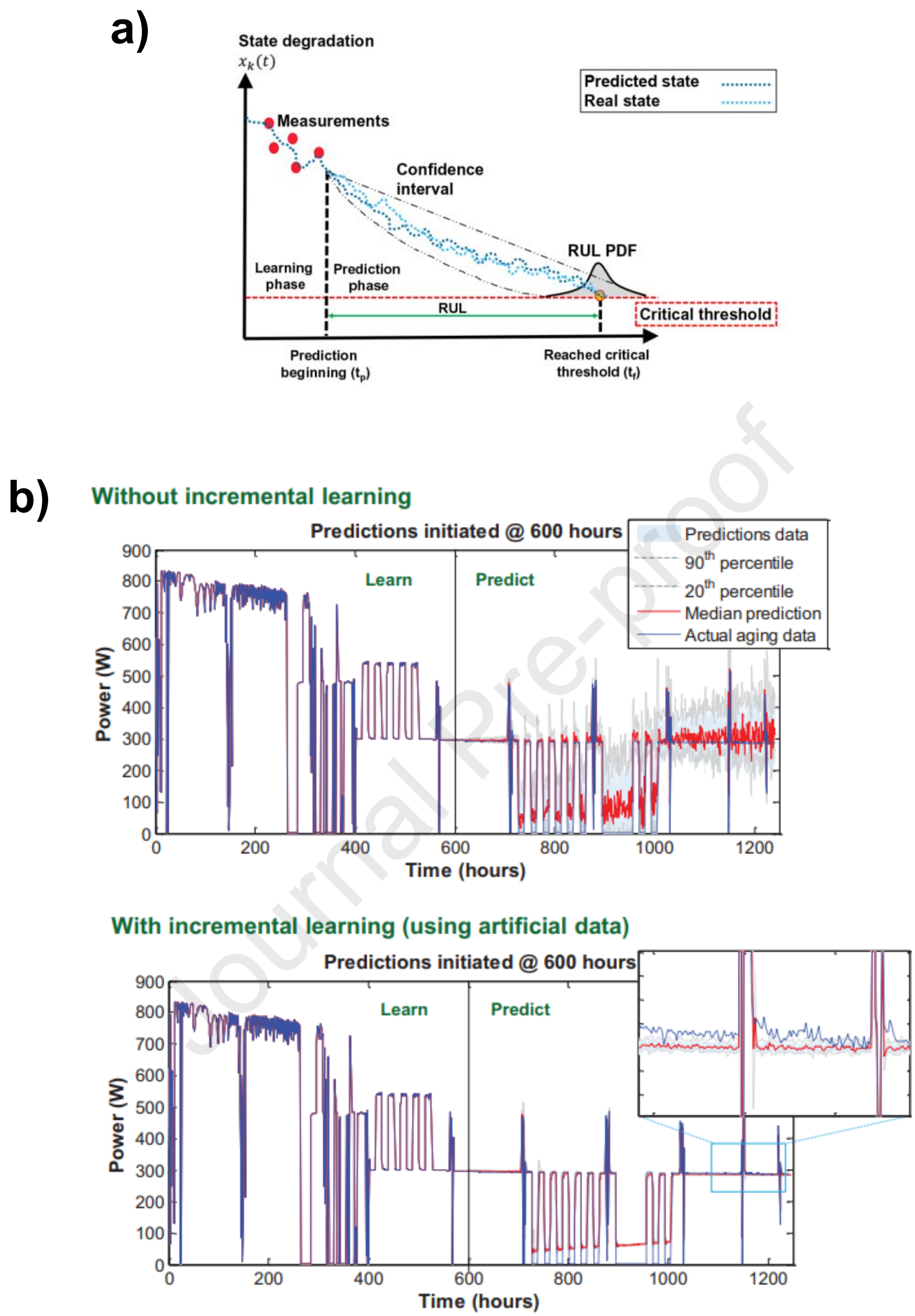


Figure 2 a) Graphical descriptions of reversible and irreversible performance degradation during a cell operation from JRC[25]. The figure was adapted from the reference.

b) Cell voltage of a commercial MEA during constant-current hold at 0.5 A·cm^{-2} interrupted by different recovery procedures[34].

c) Impact of recovery procedure on ECSA and O2 transfer resistance. Values were measured at beginning-of-test (BoT), end-of-degradation (EoD, after aging tests) and after recovery step (AR) for different MEAs[36].


a)
State degradation
$x_k(t)$
Predicted state
Real state
Measurements
Confidence interval
RUL PDF
Learning phase
Prediction phase
RUL
Critical threshold
Prediction beginning (t_p)
Reached critical threshold (t_f)
b)
Without incremental learning
Predictions initiated @ 600 hours
Predictions data
90th percentile
20th percentile
Median prediction
Actual aging data
Learn
Predict
Power (W)
Time (hours)
With incremental learning (using artificial data)
Predictions initiated @ 600 hours
Learn
Predict
Power (W)
Time (hours)

c)

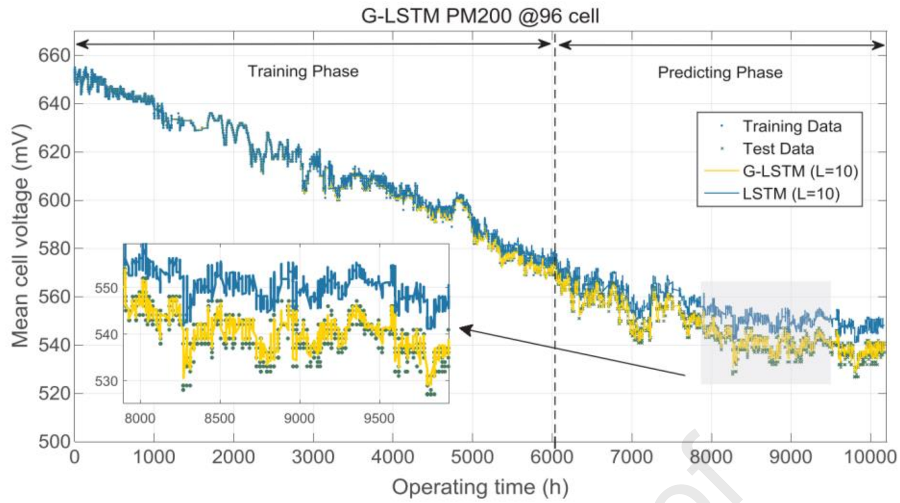


Figure 3 a) Diagrammatic description of the entire prognostic process[48].

b) The long-term prediction results of PEMFC power with and without incremental learning[45]. Incremental learning: Prognostics models are re-trained and their parameters are updated according to new data available.

c) Predicting performance comparison between G-LSTM and LSTM approaches[51]. Long short-term memory (LSTM): An artificial recurrent neural network architecture used in the field of deep learning. The LSTM cell remembers values over arbitrary time intervals and regulates the flow of information into and out of the cell. Grid LSTM (G-LSTM) is a two-dimensional architecture based on the paralleling and combining of individual LSTM cells.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: