Root cause analysis of the degradation in a unitized regenerative fuel cell

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ABSTRACT

The present study emphasizes the possible modes of failure of a unitized regenerative fuel cell (URFC) when operated in fuel cell as well as in electrolysis mode at different temperatures viz. 30 °C and 60 °C. The carbon based catalyst (Pt/C) and diffusion layers are used to characterize the degradation of the URFCs. The electrolysis mode of operation is found to dominate the root cause of failure with increase in temperature. Agglomeration and loss of catalyst along with delamination of electrode from membrane are observed. Membrane degradation owing to its structural as well as chemical damage is seen to be prominent at higher temperature. Characterization techniques such as SEM, TEM and ICP-AES confirm the study showcasing the effect.

Keywords: Regenerative Fuel Cell; Degradation; Catalyst agglomeration; Electrode delamination

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1. Introduction

Unitized regenerative fuel cell (URFC) [1] is an electrochemical device, which combines the properties of the fuel cell and an electrolyser and act as a flow battery where energy is stored in the form of hydrogen. Such a system has the potential to cater the long-term mismatch in a stand-alone renewable system [2,3]. URFCs have been tried out for commercial applications [4–7] however, technological limitations have hindered their path towards commercialization. Important limiting factors include durability of the cell, the high cost of components, operating parameters and most importantly the quality of fuel supplied [8].

Attention has been given to study degradation and its minimization in fuel cells and electrolysers individually [9–21] viz. Jing Shan et al [22] investigated the degradation of PEMFC using their own cyclic tests designed along with current density distribution system after each cycle. The methods adopted showed a decrease in electrochemical surface area (ECSA) with an increase in a number of cycles. The cracks observed at the cross-section of the membrane electrode assembly (MEA) were a clear indication of delamination of the catalyst. Rohendi et al [23] performed a detailed analysis of PEMFC degradation by which the catalyst dissolution and its oxidation along with membrane cracking and delamination were confirmed. Moreover, Nafion content used in catalyst layers played a very dominant role in fuel cell degradation [24]. Catalyst base for PEMFCs was also explored by Speder et al [25] in which Pt/C ratio was varied and tested for degradation in the accelerated test, however, a definite relation between ECSA and ratio of Pt/C could not be found. Pinhole formation using accelerated test was confirmed against the failure of MEA for PEMFC [26] wherein microporous layer (MPL) and polytetrafluoroethylene (PTFE) were seemed to be dissolved over time. As a result, Pt agglomeration was found to increase from inlet to outlet because of large pores produced. A similar study done on the impact of the pinhole on the degradation of PEMFC [27] revealed that the pinhole near inlet had more effect on the cell degradation in terms of decrement in open circuit voltage (OCV) and hydrogen crossover. Cyclic humidity and temperature have also been observed to be more significant for membrane degradation [28–34]. Effect of the water formation and its presence was deeply studied [35,36] and its effect was attributed to various degradation factors like loss of active surface area of the catalyst, ionomer dissolution and corrosion, contamination and morphological changes in MEA and gas diffusion layer (GDL). Operating under open circuit condition for an extended period could also affect the durability in

terms of oxidation of catalyst [37–39] and could be minimized if the cell is isolated from hydrogen and air source and putting a high load.

Degradation study of the various combinations of RuO₂ and Ta₂O₅ catalyst in the high temperature (150° C) PBI based PEM electrolyser were done [40] out of which 90 wt% RuO₂-wt10% Ta₂O₅ was found to be more stable than RuO₂ for 5 h at 150° C. Another study involving degradation of polymer exchange membrane water electrolyser (PEMWE) [41] indicated the membrane thinning along with catalyst precipitating inside the membrane during accelerated degradation test. Apart from the membrane, catalyst and diffusion layers [42], bipolar plates (BPPs) have been part of degradation and could be prevented by applying anticorrosive coatings on base plates [43].

Degradation study of URFC has not yet been reported despite individual attempts in fuel cells and electrolyzers. Authors, therefore, try to investigate the dependence of durability of URFC with respect to temperature over definite cycles of fuel cell mode and electrolysis mode in terms of various causes reported elsewhere.

2. Experimental method

2.1 Single cell assembly

Nafion membrane (NR-212), used as an electrolyte was initially treated with HNO₃, H₂O₂ and H₂SO₄ for the removal of any organic and inorganic impurities [44]. Gas diffusion layers (GDLs) were prepared by sintering the coated homogeneous slurry of VulcanXC-72 and PTFE (15 wt%) in isopropyl alcohol (IPA) on carbon paper (Toray-TGP-H-120) for a loading of 1.5 mg cm⁻². Finally, the electrodes were prepared by coating the mixture of platinized carbon Pt/C (40 wt%), IrO₂ and Nafion as an ionomer in IPA on GDL [45]. Loading of 0.1 mg cm⁻² of Pt/C along with 7 wt% of ionomer was maintained for hydrogen electrode whereas, 0.5 mg cm⁻² of Pt/C with 30 wt% of ionomer was used for oxygen electrode. The membrane electrode assembly (MEA) was later prepared by hot pressing the Nafion membrane between the electrodes (4.5 cm x 5 cm) at 60 kg cm⁻² at 130 °C for 3 min [46]. Finally, the MEA was placed between a pair of titanium nitride (TiN, Oerlikon Balzers) coated SS bipolar plate to avoid corrosion at the interfaces [47–49]. The assembly was clamped to confirm uniform contact pressure between electrode and BPPs to reduce the contact resistance [50,51].

2.2 *Diagnosis of degradation*

To investigate the degradation, it was important to characterize the cell with current voltage characteristics and electrochemical impedance spectroscopy (EIS) in fuel cell mode and electrolyser mode. The MEA was further taken to post-mortem in scanning electron microscopy (SEM), transmission electron microscopy (TEM) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for detailed analysis of the degradation.

2.2.1 *Electrochemical analysis*

The URFC was maintained in 30 °C and 60 °C and the performances were monitored continuously for 3 days alternatively in fuel cell mode and electrolyser mode as illustrated in Fig. 1. The cycle commenced with the conditioning of the MEA in fuel cell mode between FC_1 and FC_2, followed by supplying deionized water (DI) in accordance with the operating temperature of the cell during electrolysis mode which was extended for 8 hours in chronopotentiometry mode at 100 mA and further followed by an idle duration for 4 hours. It should, however,, be noted that the temperatures mentioned above are the ones at which electrolysis mode was operated. The current-voltage characteristics, impedance spectroscopy were performed at the points FC_2, FC_4, and FC_6, while operating in fuel cell mode as well as at the points EL_2, EL_3, EL_5 and EL_7 while operating in electrolyser mode as indicated in the Fig. 1.

Fig. 1. Schematic layout of the experimental investigation

Since the cells were supposed to be operated in fuel cell and electrolysis mode, different combinations of equipment were adopted for the experiments as presented in the Fig. 2. Polarization behaviors of the cells were carried out with the help of a fuel cell test station. However, the electrolysis mode was operated using a programmable DC power source with a separate arrangement of DI at controlled temperature and flow.

Characterization of the cell was carried out with EIS to analyze the changes in the ohmic resistance, and the charge transfer resistance for hydrogen oxidation and evolution, as well as oxygen reduction and evolution. The spectroscopy was performed in a potentiostatic mode with the frequency ranges from 1 MHz to 10 kHz at OCV conditions in both modes with an amplitude of 10 mV. Hydrogen electrode was made as a counter as well as reference electrode considering negligible overpotential for hydrogen oxidation and reduction, whereas, oxygen electrode was considered as working electrode.

Fig. 2. Schematic layout of the experimental set up (a) Impedance analyzer, (b) DC source for electrolyser, (c) fuel cell test station and (d) DI supply unit with temperature and flow controller

2.2.2 Microscopic analysis

The cross sections of the MEAs were studied with scanning electron microscopy to perform further post-mortem analysis. Elemental mapping along with the microstructural changes in the MEAs were compared with the pristine one to analyze the degradation effect. Catalyst degradation was studied with the help of Philips microscope (CM 200) at 200 kV. The Anode, as well as cathode catalyst layers, were observed for their thickness, microstructure, and distribution.

2.2.3 Spectroscopy analysis

Inductively coupled plasma-mass spectroscopy (ICP-MS) typically ionizes the metal in the solution and then uses the mass spectrometer to quantify the same with the help of separation. ICP-MS was performed on MEA which was cut out as a sample (2 cm x 1 cm) and digested in a mixture of 2 mL HCl (60 wt%), 2 mL HNO₃ (45 wt%) and 10 mL HF (40 wt%) in a microwave at 250 °C for 30 min. The filtered solution was later added with DI to make 25 mL

in total which was further analyzed to quantify the Pt and Ir concentration for which ARCOS, simultaneous ICP spectrometer (SPECTRO Analytical Instruments GmbH, Germany) was used.

3. Results and discussion

MEAs of URFCs were prepared and investigated at two different temperatures viz. 30 and 60 °C. At each temperature, the experiments were carried out for three times with three different MEAs. The average results obtained from three experiments are presented in the following sections.

3.1 Current-voltage characteristics

Characterization of the cell with current-voltage behavior was performed as an initial step towards understanding the degradation. The current-voltage behavior obtained on the different days in fuel cell mode and electrolyser mode are presented in Fig. 3a and 3b respectively. An acceleration in the degradation was observed with an increase in the operating temperature,. The degradation rate of the cell was slower when the cell was operated at 30 °C, however, the rate of degradation became severe at 60 °C and it brought down the performance of cell rapidly. Such an increment in the degradation over temperature could be attributed to oxidation of carbon during electrolysis mode, catalyst agglomeration, and catalyst oxidation, thermal, mechanical and chemical degradation of the membrane which is confirmed by further studies.

The performance comparison for EL mode has been presented in Fig. 3c and 3d and similar trends were observed with the effect of degradation. For lower temperature (30 °C), the MEA was observed to degrade at a relatively low rate and further accelerated with the increase in the temperature of 60 °C. Such a rise in the temperature causes mechanical and chemical damage to MEA because of which the every part of the cell that comes in contact with active oxygen during electrolysis mode, is prone to corrosion.

Fig. 3. Performance comparison between MEAs operated at (a) 30 °C and (b) 60 °C in FC mode; (c) 30 °C and (d) 60 °C in EL mode.

3.2 Electrochemical impedance spectroscopy analysis (EIS)

EIS was performed (Fig. 4) at each point along with I-V measurements to study the effect of the degradation at two different temperatures. Hydrogen electrode in the case of FC, as well as EL mode, is observed to have increased resistance relatively at a slower rate as compared to the oxygen electrode. This could be because of slower oxidation of carbon support on the electrode. However, oxygen electrode is prone to degradation relatively faster and could be attributed to the continuous oxidation of carbon support that led to the agglomeration of the catalyst during EL mode thus increasing the charge transfer resistance (R_{CT}) of the cell. The cyclic change in modes is seen to have an impact on FC mode in particular. The membrane resistance is also seen to increase over time pointing towards its structural as well as chemical degradation.

Fig. 4. Comparison of EIS between MEAs operated at (a) 30 °C, (b) 60 °C in FC mode; (c) 30 °C and (d) 60 °C in EL mode.

3.3 Activation polarisation analysis

The activation overpotential in the electrolysis, as well as fuel cell mode, was studied closely separately in the linear zone ($\eta \rightarrow 0$) and Tafel range ($\eta \gg RT/F$). Both FC and EL modes were typically scanned for activation overpotential viz. 0 to 130 mV and analysed first for low overpotential ($0 < \eta < 30$ mV) and for higher overpotential ($75 \text{ mV} < \eta < 135$ mV) based on Tafel plot as presented in Fig. 5 and 6 respectively. Fig. 5a and 5b showcase the linear relation between current and overpotential for FC mode over a complete cycle. In the case of low temperature of operation, the cell was seen to degrade on the third day. However higher degradation was observed over time as the slope of locus of points increased in the case of the high temperature of operation.

Fig. 5. Performance comparison in lower activation overpotential between MEAs operated at (a) 30 °C, (b) 60 °C in FC mode; (c) 30 °C and (d) 60 °C in EL mode.

Degradation was observed to be dominant in case of electrolysis (Fig. 5c and 5d) mode as the resistance of the cell is increased gradually over time and countered everything at a high temperature of operation. Tafel plot was plotted to observe the change in exchange current density. The overpotential between 90 till 130 mV is typically presented in Fig. 6. In the case of FC mode of operation, the MEA (for 30 °C) was seen to degrade on the third day which is in the agreement of Fig. 5a whereas strong degradation was observed at a higher temperature (60 °C). This proves the fact that operating temperature of electrolysis affects its durability. A similar effect is observed in EL mode confirming the dependence of cell durability over its operating temperature (Fig. 6c and 6d).

Fig. 6. Comparison of Tafel plots between MEAs operated at (a) 30 °C, (b) 60 °C in FC mode; (c) 30 °C and (d) 60 °C in EL mode.

3.4 Effect on electrochemical surface area

The total electrochemical catalyst surface area available in an electrode dictates the activation polarization behavior of the electrode which can be quantified by apparent exchange current. The relation between intrinsic exchange current density and apparent exchange current density of the hydrogen and oxygen electrodes with an electrochemical catalyst surface area, A_{ecsa} are given by following equations: [52]

$$i_{O_2}^0 = (A_{\text{ecsa}})_c i_{O_2(Pt/PtO)}^0 \left[\frac{P_{O_2}}{P_{O_2}^0} \right]^{0.001678T} \quad (1)$$

Where,

$i_{O_2}^0$ is the apparent exchange current density for O_2 reduction, $A\cdot m^{-2}$

$i_{O_2(Pt/PtO)}^0$ is the intrinsic exchange current density for O_2 reduction on Pt/PtO surface, $A\cdot m^{-2}$

P_{O_2} is the partial pressure of O_2 in feed streams, atm

$P_{O_2}^0$ is the standard pressure of O_2 , atm

T is the operating temperature, K

$$i_{H_2}^0 = (A_{ecsa})_a i_{H_2(Pt)}^0 \left[\frac{P_{H_2}}{P_{H_2}^0} \right]^{0.5} \quad (2)$$

Where,

$i_{H_2}^0$ is the apparent exchange current density for H_2 oxidation, $A\cdot m^{-2}$

$i_{H_2(Pt)}^0$ is the intrinsic exchange current density for H_2 oxidation on Pt surface, $A\cdot m^{-2}$

P_{H_2} is the partial pressure of H_2 in feed streams, atm

$P_{H_2}^0$ is the standard pressure of H_2 , atm

The total electrochemical catalyst surface areas available in the different electrodes at different points of the experiment were estimated from the above-mentioned equation and the electrochemical surface area as a fraction of its initial value is represented in Table 1. It could be observed that the decrement in apparent exchange current density (AECD) was predominantly because of a decrease in the electrochemical catalyst surface area over time.

Table 1. Variation in ECSA in FC mode at different operating temperatures

Temperature of operation (°C)	FC_2	FC_4	FC_6
30	0.92	0.81	0.5
60	0.70	0.04	0.02

EPSA or ECSA of electrodes which are the ratios of Pt surface in cm^2 to cm^2 geometrical area of the electrode; decrease attributing to a loss in active sites because of oxidation of catalyst base i.e. carbon and/agglomeration. Also, at a higher temperature of operation, water content at triple phase boundary seems to get reduced thus decreasing the active sites as Pt-covered with a thin layer of water and Nafion could be considered as the active site [52].

Moreover, a study involving loss of ECSA of Pt over time revealed relatively slow degradation when the cell was operated at 30 °C during first two cycles, followed by a severe

degradation in the last cycle. However, degradation rate was seen to be multiplied in second and third cycles of operation for 60 °C.

3.5 Microscopy study

SEM of freshly prepared MEA samples have been compared with that of degraded MEAs in Fig. 7a and 7d. The cross-sectional image of fresh MEA revealed that the membrane and electrodes are tightly bonded with each other, however, degraded MEA depicted the effect of membrane thinning along with the delamination at the interface of the membrane and the electrode. Membrane thinning could be attributed to the severe mechanical and chemical degradation that took place during electrolysis mode of operation. However, the effect of the delamination is not apparent in the polarization behavior. This could be due to the fact that when the MEA is removed from the assembly the electrode might still be in good contact with the membrane despite local delamination at places.

The other section of Fig. 7 represents the elemental mapping of the fresh and degraded MEA. Although there is not much difference observed between the respective images for Pt and Ir over the entire area, relatively dense catalyst particles could be seen in the fresh sample (Fig. 7b and 7c) along with the membrane confirming the presence of catalyst layer. The degraded MEA did not have dense catalyst layer supporting the fact of the severe losses of the catalyst at the electrodes (Fig. 7e and 7f). It should be mentioned that the difference in the appearance of the layer on both electrodes is mainly due to the higher loading at oxygen electrode in comparison to that of hydrogen electrode as discussed in section 2.1.

Fig. 7. Cross-sectional SEM image of (a) fresh and (d) degraded MEA; elemental mapping of catalysts before (b and c) and after (e and f) the study across the MEA cross section.

Images obtained from TEM are presented in Fig. 8a and b, and are compared to the size and distribution of the catalyst. More agglomeration of catalyst particles is seen in the sample prepared from MEA used for the investigation whereas relatively fine distribution is observed with that of a fresh one. This confirms the low performance of cells over time and temperature.

Fig. 8. TEM images of (a) fresh catalyst, (b) catalyst obtained from degraded MEA and (c) loss of ECSA of Pt catalyst with time with reference to the initial value.

Moreover, study involving loss of ECSA of Pt over time revealed that relatively slow degradation was observed for the cell operated at 30 °C for first two cycles, followed by severe degradation in last cycle. However, degradation rate was seen to be multiplied in second and

third cycles of operation for 60 °C. Fig. 8c showcases the degradation rates in terms of loss of ECSA of Pt over time as confirmed in Fig. 5a and b.

3.6 Spectroscopy study

In order to quantify the catalysts loss from the MEAs, ICP-AES was performed. Table 2 shows the percentage of Pt and Ir loss at end of the cycle. It could be observed that more percentage of Pt was lost at a higher temperature of operation which could be attributed to higher structural damage to the catalyst layer of MEA. However, percentage loss of Ir was observed to be similar in both the cases.

Table 2. Percentage of catalyst loss at different operating temperatures of operation.

% loss of catalyst	Temperature of operation (°C)	
	30	60
Platinum	48.3 ± 6	65.8 ± 3.5
Iridium	54 ± 10	54.3 ± 1.5

4. Conclusions

In the present study, the degradation of the unitized regenerative fuel cell is studied at 30 °C and 60 °C. From the results, it is clear that the degradation is prominent in both the temperatures, however, it accelerates with the increase in the operating temperature specially in electrolysis mode of operation. Such increase in the temperature leads to structural and chemical damage to membrane causing its thinning over time. With uneven surface as an effect of thinning in the microscopic scale, the electrodes are separated out resulting in delamination of membrane electrode assembly. However, the consequences of this is not apparent under assembled condition due to clamping pressure. The higher operating potential of the cell causes oxidation of catalyst support, carbon. With the absence of the support, catalyst agglomerates over time and gets washed out in some cases. With the increase in temperature of operation and potential, the stability, and durability of the bipolar plate also gets affected severely.

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Acknowledgement

This research is based upon work supported by the Solar Energy Research Institute for India and the U.S. (SERIUS) funded jointly by the U.S. Department of Energy subcontract DE AC36-08G028308 (Office of Science, Office of Basic Energy Sciences, and Energy Efficiency and Renewable Energy, Solar Energy Technology Program, with support from the Office of International Affairs) and the Government of India subcontract IUSSTF/JCERDC-SERIUS/2012 dated 22nd Nov. 2012.

Abbreviations

AECD	Apparent exchange current density
BPP	Bipolar plate
DI	Deionized water
ECSA	Electrochemical surface area
EPSA	Electrochemical Pt surface area
GDE	Gas diffusion electrode
GDL	Gas diffusion layer
IECD	Intrinsic exchange current density
ICR	Interfacial contact resistance
Ir	Iridium
IPA	Iso-propyl alcohol
MEA	Membrane electrode assembly
MPL	Microporous layer
OCV	Open circuit voltage
PTFE	Polytetrafluoroethylene
PEMFC	Polymer electrolyte membrane fuel cell
PCB	Printed circuit board
Pt	Platinum
R_{CT}	Charge transfer resistance
URFC	Unitized regenerative fuel cell
TiN	Titanium nitride

Figure captions

- Fig. 1. Schematic layout of experimental plan.
- Fig. 2. Schematic layout of the experimental set up (a) Impedance analyzer, (b) DC source for electrolyser, (c) fuel cell test station and (d) DI supply unit with temperature and flow controller
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Table 2. Percentage of catalyst loss at different operating temperatures

Table 1. Variation in ECSA in FC mode at different operating temperatures

Temperature of operation (°C)	FC_2	FC_4	FC_6
30	0.92	0.81	0.5
60	0.70	0.04	0.02

Table 2. Percentage of catalyst loss at different temperatures of operation.

% loss of catalyst	Temperature of operation (°C)	
	30	60
Platinum	48.3 ± 6	65.8 ± 3.5
Iridium	54 ± 10	54.3 ± 1.5