Analysis of performance degradation during steady-state and load-thermal cycles of proton exchange membrane water electrolysis cells

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Abstract

A membrane-electrode assembly based on a 90 µm short-side-chain Aquivion® proton exchange membrane and containing low catalyst loadings, 0.4 mg IrRuOx cm^{-2} and 0.1 mg Pt cm^{-2} at anode and cathode, respectively, is investigated for combined thermal and load cycling at high current density (3 A cm^{-2}) in water electrolysis cell. Durability tests under steady-state and load-thermal cycles are compared to evaluate the efficiency losses under specific operating conditions. Ac-impedance spectra and post-operation analyses are carried out to investigate the degradation mechanism. Catalyst degradation occurs more rapidly under cycled operation whereas mass transfer issues are relevant especially under steady-state mode. Membrane thinning appears to be affected by the uptime hours at high current density. The overall cell voltage increase is slightly larger for the cycled operation compared to the steady-state mode. However, this is essentially related to a compensation effect associated to a larger decrease of series resistance during the steady-state durability test. The dynamic electrolysis mode at high current density does not exacerbate significantly the degradation issues of low catalyst loading MEAs compared to a steady-state operation. This confirms the proper dynamic characteristics of the polymer electrolyte membrane electrolyser.

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1. Introduction

Electricity production from renewable sources can allow to reduce significantly CO_2 emissions and thus mitigate the effects of climate changes. The expected wide-scale diffusion of renewable energy sources will significantly contribute to the implementation of the new energy and environmental policy objectives to achieve the Paris CO21 conference targets.[1] Most of the future production of electricity is thus expected to come from renewable energy sources. However, because of the intermittent and unpredictable nature of renewable power production, an advanced energy storage is necessary to provide a proper solution for an efficient use of renewable sources such as solar plants and wind mills. [2-5] In the future, a large utilization of renewable power is expected to cause increasing energy management issues. This requires developing rapid-response, cheap and large scale energy storage systems capable of absorbing the surplus of electrical power. A large-scale energy storage will avoid relevant investments to develop a new grid infrastructure.

The excess of electricity, that cannot be transferred to the grid when there is no much request, can be utilized to produce high purity hydrogen by water electrolysis. This will allow efficient energy storage into a chemical compound acting as energy vector. Electrolysis can assist grid-balancing thus improving power quality, frequency and voltage control. In this regard, electrolysers should be designed to handle frequent start-stop cycles, dynamic operations and allow partial load operation. Specifically, electrolysers should be capable to handle variable energy input from renewable power sources locally available and have to adapt properly to the intermittent profile of electricity supply.

There are different technologies for water electrolysis: liquid alkaline electrolyte, polymer electrolyte membrane (PEM) and solid oxide electrolysers (SOECs). PEM electrolysers appear to be characterized by an appropriate dynamic behaviour and good flexibility for interfacing to renewable sources. [6-20]

In particular, proton exchange membrane water electrolysis possess the ability to rapidly follow the intermittent energy production from renewable power sources and can provide proper grid-balancing service to mitigate the differences in energy generation and consumption.

Sun et al. [21] reported a Proton Exchange Membrane Water Electrolysis (PEMWE) stack tested for 7800 h with an average degradation rate of 35 μV h^{-1} per cell. They showed that the performance degradation of the stack was mainly caused by recoverable contaminations.

Frensch et al. [22] compared the performance over time of seven different operation modes (constant current, constant voltage, current cycling, etc.) to investigate the realistic degradation responses of a PEM WE for grid balancing services. They showed different advantages and disadvantages of different operation modes in terms of performance variation over time.

Rakousky et al. [23] investigated a PEMWE single cell for 1000 h observing a significant degradation rate of 194 μV h^{-1}. They concluded that the 78 % of the detectable degradation can be explained by an increase in ohmic resistance.

Rakousky et al. [24] analysed the impact on investment costs of a PEMWE operating at elevated constant and intermittent current densities. They indicated that the PEMWE can be effectively coupled to intermittent power profiles from renewable energy sources without substantially affecting long-term stability.

In our previous works [25, 26], we have investigated the steady-state durability of PEM electrolysis cells containing different catalyst loadings. We have observed that the degradation rate is affected by the anode catalyst turn-over frequency operation. The degradation rate

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increased in the presence of high operating current densities and especially for <mark>low</mark> anode catalyst loadings.

In this work, the dynamic behaviour of a PEM electrolysis cell containing low catalyst loadings was studied in order to understand its effect on performance degradation. The cell was based on well characterized materials such as a short-side chain Aquivion membrane [26-32] and a solid solution Ir and Ru oxide catalyst at the anode (0.34 <mark>$mg\ cm^{-2}$</mark> Ir+Ru) [29, 33-35]. Two different operating conditions have been investigated using equivalent electrolysis cells. The first was operated in a steady-state condition at high current density (3 A cm^{-2}) whereas the second was subjected to load and thermal cycles. The degradation of the membrane-electrode assembly was studied by physico-chemical and morphological analyses.

2. Experimental

2.1 MEAs preparation

$Ir_{0.7}Ru_{0.3}Ox$ was used as anodic catalyst. It was synthetized by a modified Adams method [25, 29, 33]. Dry salts of metal precursors ($IrCl_4$, xH_2O and $RuCl_3$, xH_2O, Stream Chemicals) and $NaNO_3$ (Aldrich) were treated in a furnace at 500 °C for 3 min. The fused salt-oxide product was cooled down, washed, filtered and dried overnight in an oven at 80 °C. To completely remove the sodium impurities, pre-leaching in $HClO_4$ (0.1 M, 80 °C, 15 min) was carried out. This procedure provided a crystalline nanosized IrRu-oxide (Ir:Ru = 70:30 at.%). A 40% Pt/C, prepared as described in ref. [36], was used as H_2 evolution catalyst. A commercially available extruded short-side chain Solvay Aquivion® membrane (E98-09S) with an equivalent weight (EW) of 980 g eq^{-1} and a thickness of 90 µm was used as polymer electrolyte membrane separator. A catalyst-coated membrane (CCM) methodology was used for the preparation of MEAs [25]. The catalyst ink, composed of a dispersion of $Ir_{0.7}Ru_{0.3}Ox$ and Aquivion® ionomer (D98-06AS) was directly spray-coated onto the

membrane. The cathode ink, consisting in a dispersion of Aquivion® ionomer and Pt/C, was coated onto the other membrane side. The ionomer contents in the electrodes were 15% and 28% wt. for the anode and cathode, respectively. The precious metal catalyst loadings were 0.34 mg IrRu cm^{-2} (corresponding to 0.4 mg cm^{-2} IrRu-oxide catalyst loading) and 0.1 mg Pt cm^{-2} at anode and cathode, respectively. The formed CCMs (5 cm^2 geometric electrode area) were hot-pressed at 190°C, 1.5 min, 20 kg cm^{-2}. A titanium fibre mesh (Bekaert Toko Metal Fiber Co.) was used as backing layer for the anode side. A carbon paper-based diffusion layer backing (GDL 39BB SIGRACET®) was used for the cathode side. The CCMs and the GDLs were assembled in an in-house designed titanium single cell test fixture (5 cm^2 geometric area). Deionized water, milli-Q Integral, Millipore was fed to the anode compartment with a flow rate of 1 mL min^{-1}cm^{-2} and recirculated at the same temperature of the cell. The water resistivity measured at the cell inlet was 18.18 MΩ. Before carrying out the initial polarisation measurements, a pre-conditioning procedure at 0.05 A cm^{-2} for 24 h was carried out for each MEA to favour membrane and catalyst layers hydration and stabilisation of catalysts' oxidation state. Two equivalent MEAs were subjected to different durability tests under steady-state (1000 h) or mixed dynamic conditions (740 h).

2.2 Electrochemical characterization

The electrochemical measurements were performed at 80°C. Polarisation experiments were carried out by using a computer-controlled power supply module (TDK GEN 25-400-MD-3P400). Polarization curves were recorded in the galvanostatic mode by registering the cell voltage vs. the imposed current. At least three sets of polarisation curves were carried out under each condition to confirm data reproducibility (two in ascending mode, i.e., from the open circuit voltage to the highest current, and one in descending mode, i.e. from the highest current to the open circuit

voltage). Electrochemical impedance spectroscopy (EIS) was performed with an Autolab PGSTAT-30 potentiostat/galvanostat (Metrohm) equipped with a 20 A current booster and FRA (frequency response analyser). Electrochemical impedance analysis was carried out in the potentiostatic mode at 1.5 V and 1.8 V. The frequency was varied from 100 kHz to 100 mHz (10 points per decade) in the single sine mode with a sinusoidal excitation signal of 10 mV rms. The steady-state test was recorded in galvanostatic mode at 1 A cm^{-2} for 200 h and 3 A cm^{-2} for 800 h 1000 h in total) with a cell cut-off voltage of 2.1 V (Fig. S1, supplementary material).

Specific protocols were used in order to test the MEA response under harsh conditions with high and low frequency load variation and under thermal cycles (Figs. S2, S3). For the load cycles at 80 °C, MEA conditioning steps of 24 h at 1 A cm^{-2} and 100 h at 3 A cm^{-2} were carried out before starting the current density (load) cycling test (Fig. S2). After the two initial steady-state steps, the cell was subjected to a first cycling procedure i.e. 9000, load cycles, consisting of 10 s at 0.2 A cm^{-2} (~ 6% of nominal load) and 10 s at 3 A cm^{-2} (partial - nominal load operating) for a total duration of 50 h (Fig. S2). A steady-state operation of 50 h at 3 A cm^{-2} preceded the second cycling procedure i. e. 9000 on-off cycles of 10 s at 0 A cm^{-2} and 10 s at 3 A cm^{-2} for 50 h (warm-start simulation). Another steady-state test of 50 h at 3 A cm^{-2} preceded the third cycling procedure. This regarded 45000, on-off cycles at high frequency, i.e. 2 s at 0 A cm^{-2} and 2 s at 3 A cm^{-2} for 50 h (Fig. S2). The fourth cycling step, on-off cycles at low frequency, was equivalent to the previous one but the cell was kept for 30 min at 0 A cm^{-2} and at 3 A cm^{-2} for 50 h with 50 cycles in total (low frequency cycling). The load cycling test ended with a 50 h steady-state at 3 A cm^{-2} (Fig. S2). The duration of the specific load cycling test was 530 h (Fig. S2).

This dynamic test protocol was designed to i) carry a load cycling in a wide load range, i.e. from 0.2 to 3 A cm^{-2} (from about 6% to 100% load), at an intermediate frequency (0.1 Hz), ii) evaluate warm-start up (from zero current to 3 A cm^{-2} with pumps on and nominal temperature

on) at intermediate frequency, iii) assess warm-start up at relatively high frequency (0.5 Hz), iv) assess warm-start up at relatively low frequency (~ $5 \cdot 10^{-4}$ Hz). The high frequency step was dealing with a specific grid balancing service condition (grid stabilization against spikes). These characteristics for the electrolyser dynamic behaviour assessment were derived after an analysis of the power fluctuations associated to wind mills operation in winter in north-Europe (EU H2020 FCH JU, HPEM2GAS project). [37]

In a subsequent test, the same cell was subjected to both load and thermal cycles (220 h) to simulate a cold start-up (Fig. S3). Seven steady-state steps including different temperatures and current densities were applied. The first steady-state step was for 24 h at 0 A cm^{-2} and 25 °C, followed by 24 h at 3 A cm^{-2} and 80 °C, and thereafter a steady-state of 72 h at 1 A cm^{-2} and 25 °C. The successive steps were 24 h at 3 A cm^{-2} and 80 °C with intervals of 24 h at 0 A cm^{-2} and 25 °C.

A cold start procedure was assessed in this steady-state test, combining load and thermal cycles protocol (Fig. S3) passing from the first to the second step. In the third step, a partial load operation at low temperature was simulated. The next steps have regarded cold start-up cycles. The cycling procedure, carried out in the last 210 h, has dealt with tertiary reserve energy storage.

The two protocols reported in figs S2 and S3, load cycles of 530 h and combined thermal-load cycles 210 h (dynamic operation), were applied in sequence to evaluate the effects of steady-state operation, load cycles and thermal cycles in order to simulate practical operation of an electrolysis system in grid-balancing applications. The overall dynamic test was thus lasting about 740 h. As discussed earlier, an equivalent cell was subjected to a simple steady-state operation at 1 A cm^{-2} for 200 h and 3 A cm^{-2} for 800 h (Fig. S1) to compare degradation under dynamic and steady-state operation.

2.3 Morphologic and surface analyses

Morphological and surface characterizations were carried out on both fresh and used MEAs. Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray (EDX) analysis was carried out by a FEI XL30 SFEG microscope. The instrument was operated at 25 kV and the EDX probe was used to determine the bulk elemental composition of the anode electrodes before and after the durability tests.

The morphology of the IrRuOx and Pt/C electrodes was investigated by transmission electron microscopy (TEM) using a FEI CM12 instrument. The specimens were prepared by ultrasonic dispersion of the electrode in isopropyl alcohol and subsequently depositing a drop of the suspension on a carbon-coated copper grid. The surface composition of the IrRu oxide-based anodes, before and after durability tests including the overall dynamic test consisting of both load and thermal cycle tests, was investigated by using a Physical Electronics (PHI) 5800-01 X-ray photoelectron spectrometer (XPS).

A monochromatic Al Kα X-ray source was used at a power of 300 W. Spectra were obtained with a pass energy of 58.7 eV for elemental analysis (composition) and 11.75 eV for the determination of the chemical species. The pressure in the analysis chamber of the spectrometer was 1×10^{-9} Torr during the measurements. Spectra were collected at a photo-electron take-off angle of 45° with respect to the sample surface.

3.   Results and discussion

3.1 Electrochemical characterization

A polarization curve at 80 °C and ambient pressure of the fresh PEM electrolysis MEA based on an $Ir_{0.7}Ru_{0.3}Ox$ anode and a 40% Pt/C cathode electrocatalysts and extruded Aquivion® membrane (E98 09S) is shown in Fig. 1. The overall precious metal catalyst loading was 0.44 mg cm^{-2}_{MEA} (Fig. 1a). The range of current density here investigated varied between 0 to 4 A cm^{-2}. Different sets of

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polarisation curves were carried out to confirm data reproducibility. A comparison of polarisation curves, both in ascending mode, as well as polarisation curves carried out in ascending and descending modes are shown in Fig. S4a-b. No significant deviation or curve hysteresis was observed (standard deviation was < 5 mV for each data-point of the overall polarization data-set). At 80 °C, a current density of 3 A cm^{-2} was obtained at 1.82 V with a voltage efficiency of 81 % with respect to the high heating value (HHV) of H$_2$. Operation at high current density allows a significant reduction in capital costs of the PEM electrolysis system [25, 26]. However, being the price of green hydrogen also affected by the cost of renewable energy, operation at high voltage efficiency is also particularly relevant. A nominal load of 3 A cm^{-2} represents a good trade-off for these MEAs [25].
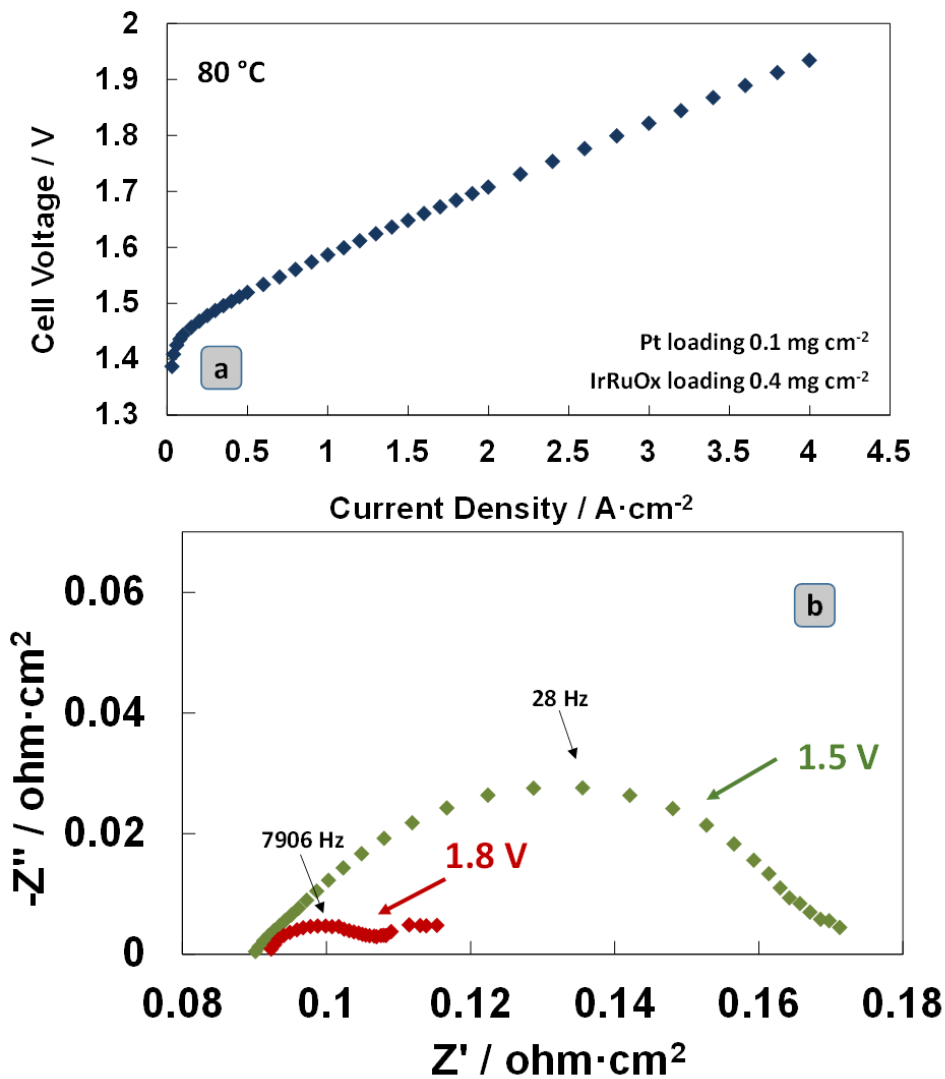
Fig. 1 (a) Polarization curves at 80 °C and (b) ac-impedance spectra at 1.5 V and 1.8 V for the fresh PEM electrolysis MEA.

Electrochemical impedance analysis was carried out under two constant cell voltage conditions, i.e., 1.5 V and 1.8 V, and reported in terms of Nyquist plots in Fig. 1b. The ac-impedance spectra in the low voltage region (1.5 V) show a series resistance (high frequency intercept on the real axis) of 90 mOhm cm^2 and a polarisation resistance (difference between low and high frequency intercepts) of 81 mOhm cm^2 at 80 °C. At high cell voltage (1.8 V), a similar series resistance was recorded (92 mOhm cm^2), whereas a lower polarization resistance, of 23

mOhm cm^2 was observed. The series resistance is manly associated to the membrane contribution

and it dominates the overall polarization behaviour at high cell voltages. In particular, the role of

the membrane is significant (>75% contribution) at a high current density of 3 A cm^{-2}. Assuming an

optimal electronic percolation in the catalyst layers and current collectors, this means that at high

currents the differential resistance in the polarisation curves is manly determined by the

membrane resistance.
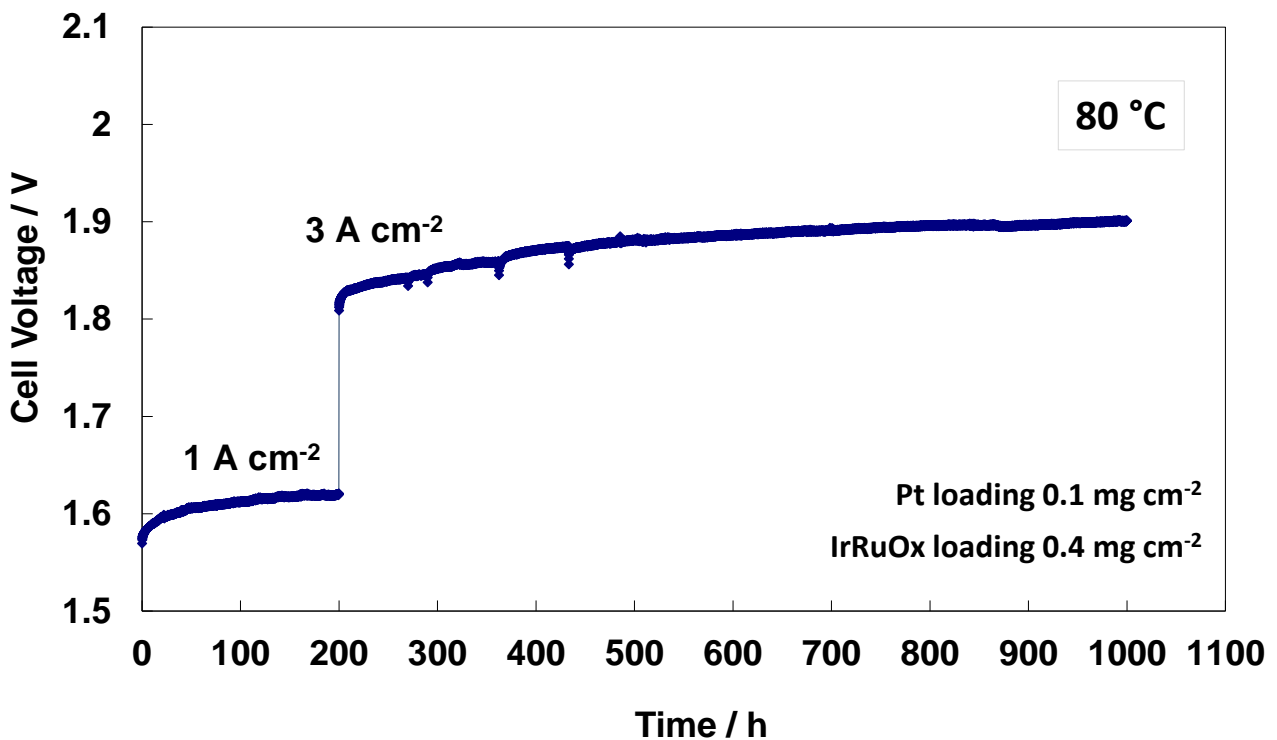
Fig. 2 MEA steady-state durability test at 1 and 3 A cm^{-2} and 80 °C

A steady-state durability test was initially carried out at 1 A cm^{-2} for 200 h; thereafter, the

current was switched at 3 A cm^{-2} for 800 h (Fig. 2). The overall steady-state test was thus lasting

1000 h. The first 200 h at low current density were appropriate for conditioning the electrolysis

cell.

A sudden increase of the cell voltage was initially observed after the initial current switch.

Similarly, a rapid increase of voltage with time was evident after the cell switch at higher current

density (3 A cm^{-2}). In general, stabilisation of cell voltage does not occur immediately when a

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significant increase of the operating current density is operated [26, 38]. This could be possibly ascribed to two main phenomena occurring under electrolysis conditions i.e. a mass transfer polarisation or a modification of the oxidation state at the anode surface according to the operating potential window (see below).

The performance decay that has been registered in the overall test at 3 $A\ cm^{-2}$ was about 90 µV/h (considering the overall time window). However, the degradation rate reduced progressively to 33 µV/h in the last 300 h of operation at 3 $A\ cm^{-2}$. As observed, the increase of cell voltage appears to be affected, to some extent, by recoverable losses. These are in part recovered by decreasing to zero the operating current (rest interval).

The occurrence of reversible losses possibly associated to mass transport issues have been discussed in the literature [39]. In the PEM electrolysis case, mass transfer issues are not much related to the provision of water at the interface being the ionomer in the catalyst layer highly hydrophilic but to the accumulation of the evolved gases in the catalyst micropores forming a diffusion barrier for the produced gas to escape from the catalytic layer. In other words, recoverable losses may be possibly related to an entrapping effect of the evolved gases in the catalyst micropores and to the gas supersaturation in the catalytic layers [39]. In fact, the occurrence of such supersaturation of dissolved gas in the catalyst layer seems to originate from mass transfer limitations during operation [39]. According to Trinke et al., this has been recognised also as the driving force of gas cross-over [39]. According to Schalenbach et al. [40-41] high saturations hinder the gas transport and thus lead to an increase of local pressure. This was also suggested by Bessarabov et al. [42]. Evidence of supersaturation of oxygen in acidic water electrolysis was further reported by Shibata and Kikuchi et al. [43-44].

However, beside all these evidences, another important phenomenon should be considered. This regards the modification of the oxidation state at the anode catalyst surface, according to the

operating potential window, during the cell switch from OCV (or low current density operation) to a high current density electrolysis mode and reverse. It is well-established that oxygen evolution reaction (OER) activity is closely linked to the nature of the IrRu-oxide species at the surface and an excursion at lower potentials could regenerate the catalyst. When the cell is under OCV, the anode is not subjected to highly oxidizing conditions, as during operation, and its oxidation state could change. Thus, less oxidising conditions may affect the anode surface and modify its catalytic properties.

Literature reports using near ambient pressure X-ray photoelectron spectroscopy for in situ monitoring of the surface state of membrane electrode assemblies during water splitting, have shown, with particular regard to $Ir_{0.7}Ru_{0.3}O_2$ anodes, that oxygen evolution occurs through a surface Ru(VIII) intermediate [45]. With regard to the iridium catalytic sites, Ir III/IV oxides/hydroxides have been detected by operando near-ambient pressure X-ray photoelectron spectroscopy on membrane-electrode assemblies [45]. During electrolysis operation, oxidation of Ir III appears to leave behind a layer of Ir IV oxides/hydroxides, which dominates the surface during the oxygen evolution process [46].

Regarding the Pt/C cathode, during an OCV interval, this is initially in contact with some residual hydrogen; but, with progressive exposure to air, it can undergo to a slight oxidation on the surface [47] with the occurrence of PtO. However, the main effect on the cell performance appears to be produced by a change of the oxidation state at the anode during the rest interval being the OER the rate determining step.
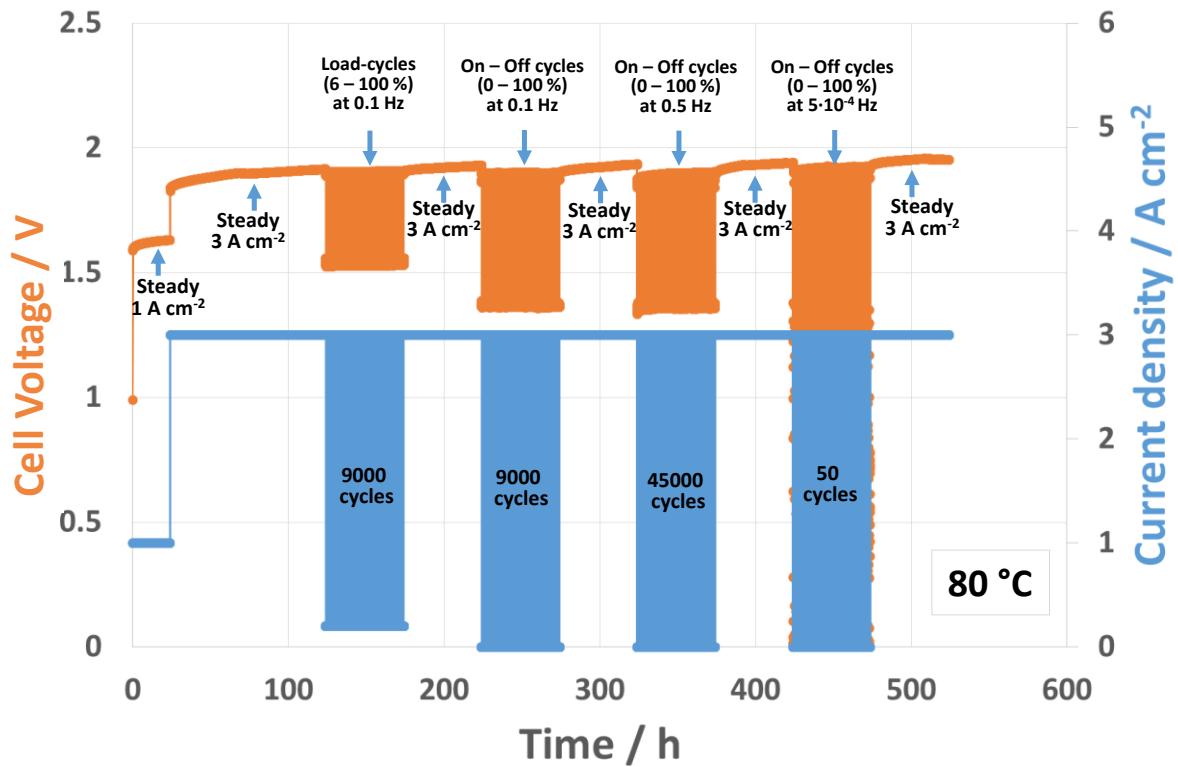
Fig 3 MEA current density (load) cycles at 80 °C; Pt loading: 0.1 mg cm^{-2};

IrRuOx loading: 0.4 mg cm^{-2}

A current density (load) cycling (530 h) test of the electrolysis single cell, carried out according to the protocol illustrated in Fig. S2, is reported in figure 3. An initial performance decay was observed when the cell was operated at fixed current (Fig. 3), but a lower decay was observed during cycled operation steps both when the minimum load was 6% or 0%. This indicates that a periodic decrease of the operating current density can mitigate performance losses (the cell potential appears to decrease slightly), although it might solely produce a recover of reversible degradation. A lower reversible cell degradation is therefore foreseen during cycled operation in grid balancing service. Interestingly, the recovery of reversible losses is larger when the frequency of the cycles and the current density window are increased. After the load cycles, the same MEA was subjected to a combined load and thermal cycles 210 h protocol (between 25°C and 80°C, at different current densities i.e. 1 and 3 A cm^{-2}). The results are shown in Fig. 4. No relevant additional performance decay during the procedure combining thermal cycles and current density

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cycles was observed. Excluding the first 100 h, the cell voltage increase was about 95 μV/h during the overall load cycles test and almost 0 μV/h during the successive thermal/load cycles.
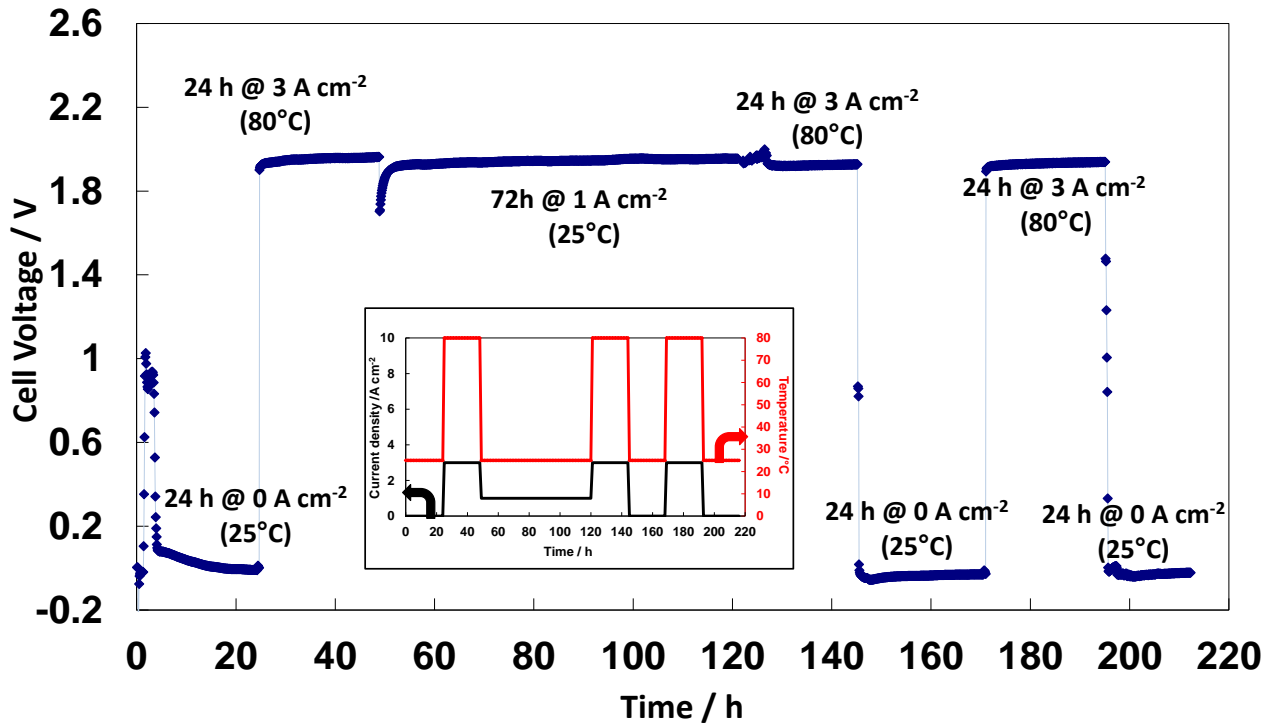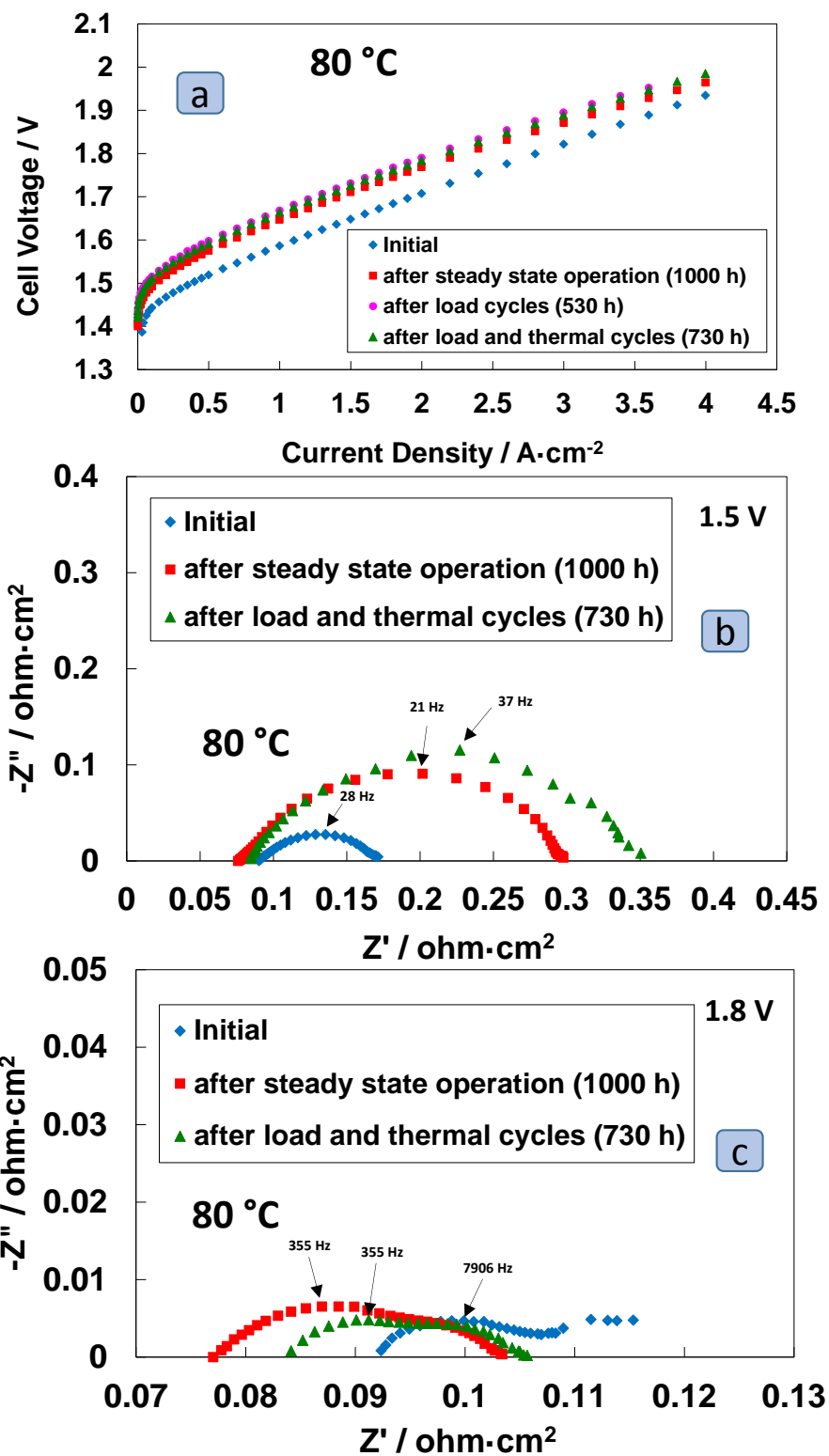

Fig. 4 Temperature and current cycling of the PEM electrolysis MEA; the test protocol is shown in the inset; Pt loading: 0.1 mg cm^{-2}; IrRuOx loading: 0.4 mg cm^{-2}

Fig. 5 MEA polarization curves (a) and impedance spectroscopy at 1.5 V (b) and 1.8 V (c) before and after steady-state durability and cycle tests; Pt loading: 0.1 mg cm^{-2}; IrRuOx loading: 0.4 mg cm^{-2}.

To confirm data reproducibility in polarization tests, various sets of polarization curves were carried out under each condition. The standard deviation in the polarization curves was < 5 mV for each data point of the overall data-set at the beginning of life and < 4 mV after the durability tests.

Thus the loss of efficiency associated to the increase of cell voltage appears more evident during the initial (530 h) load cycles, than in the successive thermal/load cycles (210 h). Moreover the steep increase of potential upon a current density switch is generally larger when the temperature is low (25 °C) than at 80 °C. These evidences indicate the occurrence of recoverable or reversible losses especially at 3 $A\ cm^{-2}$. Thus, the cell voltage increase is, at some extent, mainly associated to reversible losses. As discussed above, these are probably arising from mass transfer issues caused by gas evolution [48-49] or by a modification of the anode oxidation state according to the specific operating potential window [45-46]. In principle, zero-current intervals or cell shut down can allow to recover part of the voltage increase. It is considered that upon cell shut down, the gas molecules entrapped in the catalysts micro-pores can escape leaving the pores empty or the excursion at lower potential could regenerate the catalyst. Both phenomena, results in much lower mass transfer or kinetic overpotentials when the current is again switched from 0 to 3 $A\ cm^{-2}$. During continuous operation at 3 $A\ cm^{-2}$, the evolved gas can not escape easily from the pores because of the occurrence of a supersaturation effect [50] producing an increase of local pressure. Bessarabov et al. [42] and Schalenbach et al. [40-41] have suggested that high saturations hinder the gas transport thus leading to an increase of local pressure. This possibly causes an increase of cell voltage according to the Nernst law [51]. Both phenomena i.e., change of catalytic activity due to a variation of the catalyst oxidation state and mass transfer issues caused by supersaturation with an increase of the local pressure may have a different impact in determining the overall reversible losses. This would require specific studies including in situ spectroscopic analysis to single out which of these phenomena is the most relevant one.

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A comparison of the polarization curves and impedance spectra for the fresh MEA and the MEAs subjected to steady-state operation (1000 h), to load cycles (530 h) and to combined load and thermal cycles (210 h) is reported in figure 5. An increase of the cell voltage onset after both steady-state and cycling test procedures, is evident from the polarization curves (Fig. 5a). No particular difference between 530 h load cycles and the successive combined 210 h load and thermal cycles is observed. It is pointed out that the combined 210 h thermal-load cycles procedure has been carried out just after the 530 h load cycles procedure.

In general, the cell voltage increase in the polarization curves is slightly larger after the cycling procedure than after the steady-state operation. The effect is less evident at high current density. In terms of efficiency, at 3 $A\ cm^{-2}$, the cell voltage in the polarization curves increases by 50 mV (steady-state) and 70 mV (overall load and thermal cycling) with the respect to the initial value. In particular, at 3 $A\ cm^{-2}$, the voltage efficiencies with respect to the high heating value (HHV) are 79 % and 78 % after the overall 1000 h steady-state and the total 740 h load and thermal cycles tests, respectively.

The increase of the cell voltage onset after each test is mainly associated to an increase of polarization resistance at low frequency, quite evident in the impedance spectra at 1.5 V (Fig. 5b). This increase of cell voltage may be in part associated to a catalyst degradation.

Ac impedance analysis at 1.8 V (Fig. 5c) clearly shows a decrease of the series resistance for both steady-state and load/thermal cycle tests compared to the fresh MEA. This was essentially due to a slight thinning of the polymer electrolyte membrane as evidenced by post-operation SEM analysis of the MEA cross section (see below). It is interesting to note that the series resistance of the MEA operated under fully steady-state condition (1000 h) is lower than that of the MEA subjected to the cycled operation (740 h). Thus, membrane thinning is essentially affected by the number of uptime hours at high current density. Moreover, the polarisation resistance at 1.8 V is

smaller for the MEA operated under cycling conditions than under steady-state. This result does not appear to be aligned to the impedance response at 1.5 V where the polarisation resistance is larger after the cycles. However, it should be pointed out that the spectra at 1.5 V reflect the activation region and thus the catalyst behaviour mainly. Whereas at 1.8 V (high current density region) both reaction kinetics and mass transfer issues are reflected in the ac-impedance response. Two semicircles are clearly observed at 1.8 V. The one at low frequency is usually affected by mass transport issues [52]. This second semicircle is more evident in the ac-impedance spectra of the MEAs subjected to durability studies compared to the fresh MEA (Fig. 5c). Moreover, comparing the MEA subjected to dynamic operation and the one operated under steady-state conditions, the low frequency semicircle is more relevant in the latter one. At high current density, the diffusion constraints related to the evolution of the produced gases are more critical when continuous electrolysis operation is applied. On the other hand, during the cycles protocol, when lower or no electrical current is applied, the MEA can in principle recover part of the reversible losses occurred during the previous electrolysis operation period at high current density. In other words, the gases entrapped in the catalyst micro-pores can have sufficient time during the rest interval between two high current density steps to escape. Thus, at the beginning of a new electrolysis step at high current density, after a rest interval, a lower hindering effect towards gas evolution occurs until the gas is re-accumulated again in the micro-pores.

The significant decrease of the cell series resistance at 1.8 V in the MEA that has operated under steady-state for 1000 h, compensates for the large polarisation losses which appear critical under continuous operation at high current density (Fig. 5c). Thus, the overall impedance is slightly larger after the cycled operation compared to the fully steady-state test. At 1.8 V, the shift of the series resistance to lower values for the used MEAs compared to the fresh MEA causes an overall impedance (low frequency intercept) in the latter slightly higher than the used MEAs. This

corresponds to a higher differential resistance at high currents (3-4 $A\ cm^{-2}$). Accordingly, at high current density, the slope of the polarization curves is higher in the case of the fresh MEA with respect to the used MEAs (Fig. 5a).

However, being the overall impedance of the used MEAs at 1.5 V much higher than the fresh MEA, their cell voltage increase in the activation region (e.g. until 0.2 $A\ cm^{-2}$) is significantly larger. This reflects on the overall polarization curves, not in terms of slope but in terms of overall cell voltage increase. By comparing the impedance spectra at 1.5 and 1.8 V, one can say that, on a comparable time scale (1000 vs. 740 h), the cycles have a major impact on catalyst degradation whereas the steady state operation causes larger reversible losses and more membrane thinning effect.

3.2 Morphological and surface characterization

To better understand the degradation mechanisms, ex-situ post-operation analyses were carried out on a fresh MEA and used MEAs. Scanning electron microscopy (SEM) of the MEAs cross-sections are reported in Figure 6. A good adhesion of the electrodes to the membrane was observed in both fresh and used MEAs (Fig. 6a-c). However, the SEM cross-sections of the used MEAs show some loss of the outer anode catalyst layers (Fig. 6b). This because some outer anode layers of the used MEAs were in part transferred to the diffusion layer backing (Ti mesh) in contact with the anode during the disassembly of the cell. Whereas the cathode layer that was in contact with the carbon-based GDL was not affect by the disassembling procedure. No significant change in the morphology of the catalytic layers was recorded both after the steady-state and load and thermal cycles tests. A slight thinning of the membrane was evident after both durability tests, with the MEA operated under steady-state conditions showing the thinnest membrane. This was in agreement with the observed series resistance decrease in the impedance spectra (Figs. 5b-c). The membrane thickness varied from 90 ± 2 μm in the fresh sample to 84 ± 3 μm in the sample

subjected to load and thermal cycles and to 81 ± 3 µm in the MEA operated under steady-state

conditions (Fig. 6a-c).
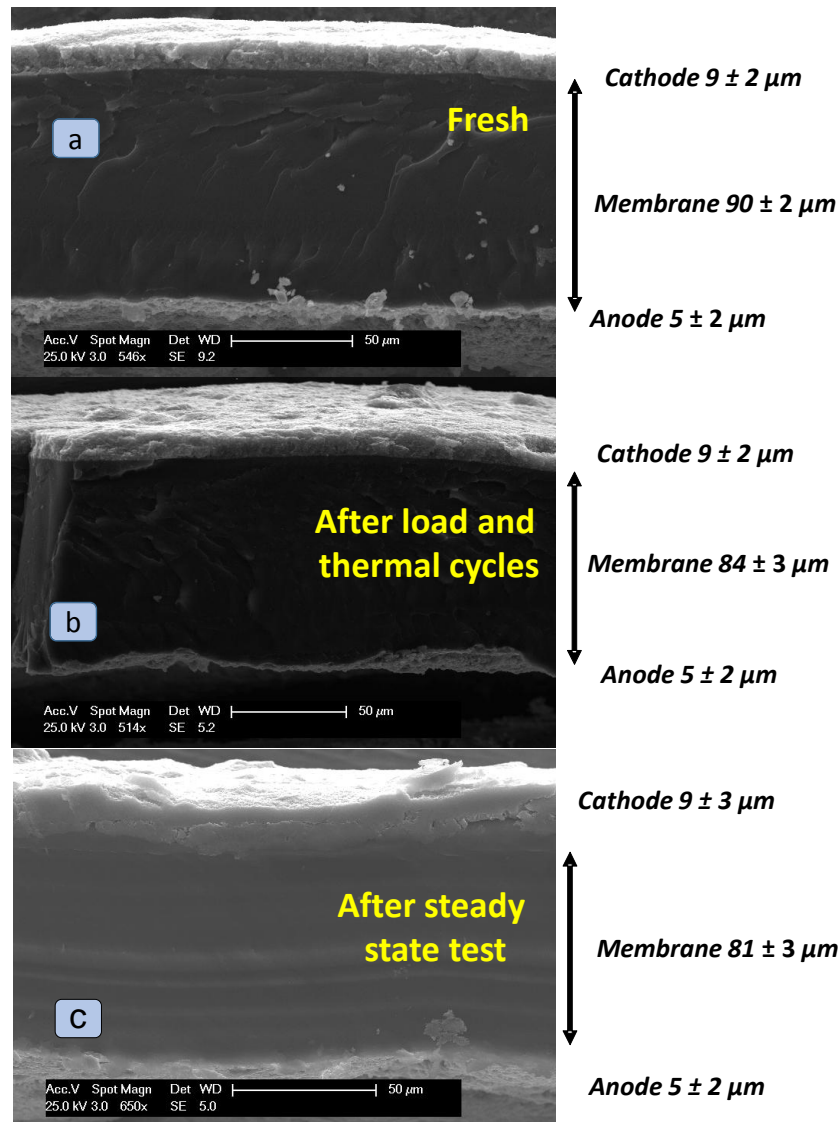
Fig. 6 SEM Cross-sections of fresh (a) and used MEAs subjected (b) to combined 740 h load and

thermal cycles (c) and to 1000 h steady-state electrolysis operation (the cathode layer is shown on

the top for all MEAs)

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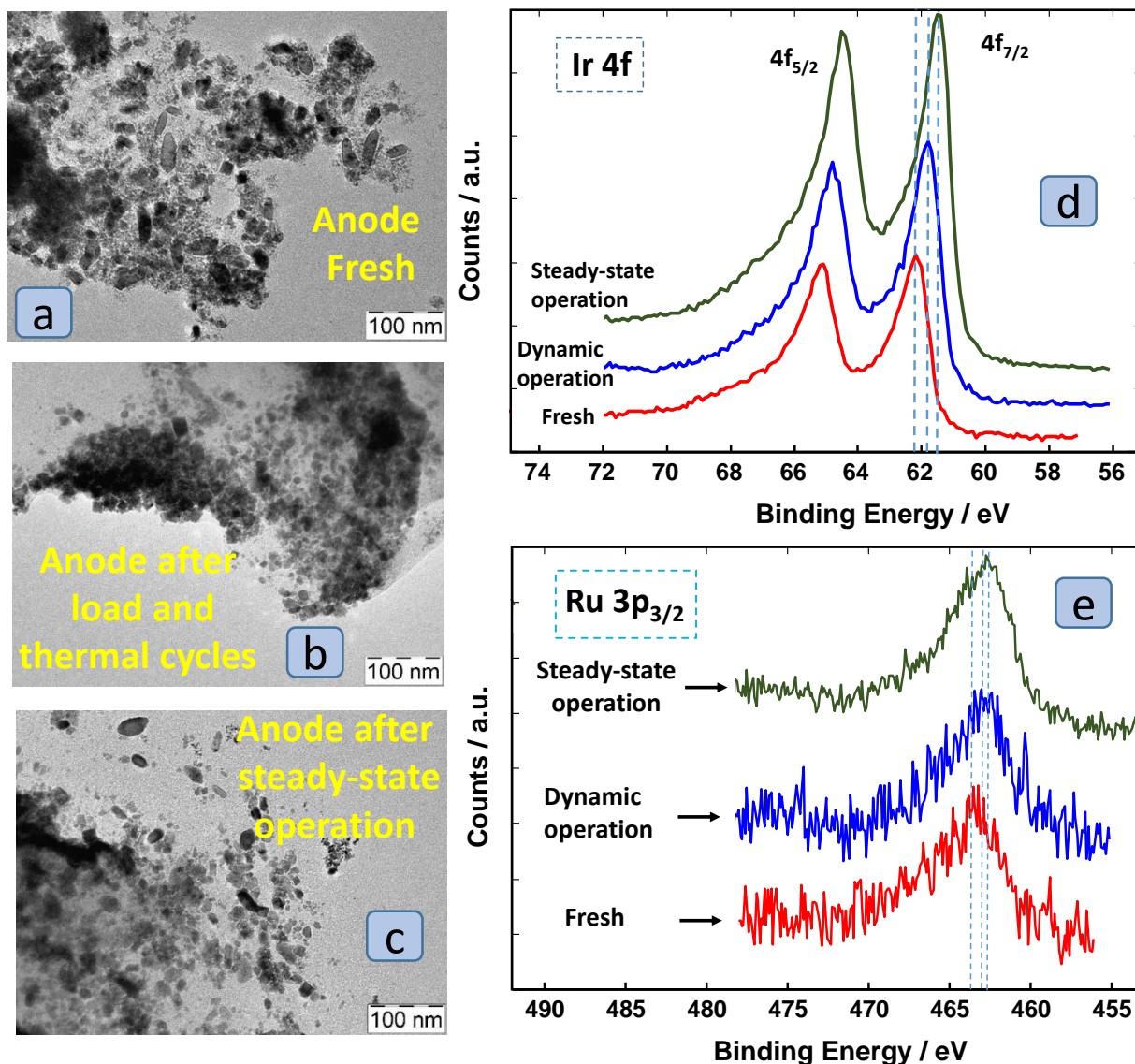
Fig. 7 TEM images for the fresh anode (a), the anode after 740 h load and thermal cycles (b), and the anode after 1000 h steady-state operation (c); high resolution Ir 4f (d) and Ru $3p_{3/2}$ (e) XPS analyses before and after the 740 h combined electrolysis cycling tests (dynamic operation) and 1000 h steady-state operation.

Figure 7a-c shows the TEM images of the anode layer for fresh and used MEAs. The anode was composed of both IrRu-oxide nanoparticles and Aquivion ionomer. The IrRu-oxide anode morphology shows a mixture of nanosized irregularly shaped and faceted particles (Fig. 7a). For what concerns the faceted particles, squared and rectangular (rod-like) shape nanocrystals are

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quite evident. The ionomer is well evident in the used samples. After the cycling test, the anode layer appears to be slightly less agglomerated than in the case of the fresh anode. Probably the reaction interface was extended by cycled electrolysis operation (infiltration of ionomer inside the catalyst agglomerates) as also observed after the steady-state operation. This phenomenon has been also observed in previous durability tests [26]. Post operation analysis of similar PEM MEAs subjected to steady-state tests and the related degradation mechanisms have been reported in previous works [25, 26].

XPS analysis was carried out on the anodic surface of a fresh MEA and used MEAs. Fig. 7d-e compares fresh and used MEAs. The Ir4f and Ru3p$_{3/2}$ photoelectron lines were selected for qualitative and quantitative analysis of the relative surface concentrations of Ir and Ru (Table 1). By comparing the B.E. of Ir 4f peaks, a shift to lower B. E. upon both steady-state operation and thermal and load cycling is quite evident (Fig. 7d). The shift of Ir 4f towards lower B.E. is more relevant for the MEA operated under steady-state than the one operated under dynamic mode (Fig. 7d).

A detailed analysis of the Ir 4f region (Fig. 7d; Fig. S5a-c, Table S1) indicates an increasing occurrence of sub-stoichiometric Ir^{3+} species for the anode surface upon 1000 h steady-state operation and 730 h cycling. This could be due to the presence, in the used sample, of iridium sites having unsaturated coordination with oxygen species; in other words, a sub-stoichiometric Ir-oxide is formed upon both steady-state operation and cell cycling. Whereas the Ir signal of the fresh anode shows a higher binding energy, entirely corresponding to Ir^{4+} in the IrO$_2$ structure compared to the used anodes. Fig. S5a-c provides a comparison of the deconvoluted Ir 4f spectra for all the three MEAs here investigated i.e. fresh MEA and used MEAs. The occurrence of an increased concentration of Ir^{3+}species, at lower binding energies, in both used MEAs compared to

the fresh MEA is confirmed. In fact, an additional peak at lower B.E. occurs upon operation; this peak is larger in intensity after continuous operation compared to the dynamic mode.

A shift of Ru3p$_{3/2}$ peak to lower binding energy for the used anodes is also evident (Fig. 7e, S6). Thus, the same phenomena occurring for Ir, are also registered for the Ru sites present on the surface of the used sample (Table 1).

It is derived that both electrolysis cycles and prolonged steady operation can cause an extraction of oxygen from the Ir-Ru-oxide with the formation of a substoichiometric Ir-Ru oxide phase on the surface [25, 26]. The atomic Ir/Ru ratio on the surface slightly varied upon cycling from 75 at. % Ir and 25 at. % Ru in the fresh anode to 80 at. % Ir and 20 at. % Ru after cycled operation whereas this metal ratio did not change substantially after the steady-state operation (Table 1) in accordance with what observed in our previous durability tests [25, 26]. A bulk energy dispersive X-ray analysis (Table 1) also shows a slight loss of Ru from the anode operated under dynamic mode (a typical EDX spectrum of the cycled anode is shown in Fig. S7). Beside the presence of a sub-stoichiometric oxide phase on the anode surface, the slight loss of Ru species may represent another cause of catalyst performance degradation especially associated to cycled operation as observed in the impedance spectra collected in the activation region of the polarisation curves (Fig. 5b).

TEM images of the cathode layer for the fresh and cycled MEAs are reported in Fig. 8a-c. The Pt/C catalysts are embedded into the Aquivion® ionomer layer. A very slight growth of the Pt particles upon cycled operation is observed. Similar evidence is observed after the steady-state test (Table 1). However, although this slight cathode sintering may contribute to some catalyst performance degradation, the degradation phenomena observed for the anode appear more relevant being this process the rate determining step in the activation region [44]. The anode

degradation is essentially considered the main responsible of the increase of polarization resistance in the low cell voltage region.
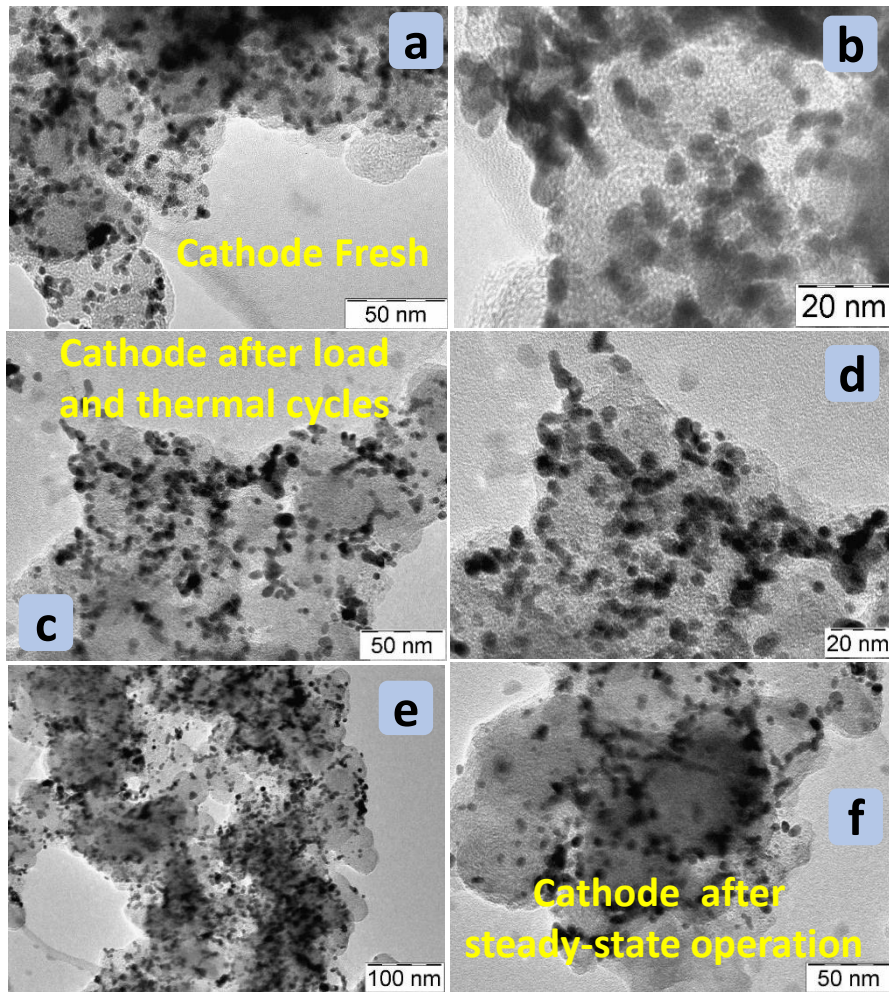
Fig. 8 TEM images for the fresh MEA cathode (a-b), the MEA cathode after 740 h load and thermal cycles (c-d), and the MEA cathode after 1000 h steady-state durability test (e-f).

The results of the ex-situ physico-chemical analyses are summarised in Table 1. The main changes, observed for the used MEAs compared to the fresh one, are a slight thinning of the membrane and the presence of substoichiometric oxide species at the anode. Both phenomena are more evident after the steady-state durability test. Both bulk and surface elemental compositions (EDX and XPS analyses, respectively) for the metals involved in the anode do not vary significantly after the steady-state operation but some losses of Ru are envisaged after the dynamic operation. The

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mean catalyst particle size appears not much affected by the durability tests for the anode and just in a modest extent for the cathode.

Table 1. Survey of main results from ex-situ physicochemical analysis

	Membrane thickness	Bulk elemental analysis of Ir and Ru metals in the anode layer SEM-EDX		Surface elemental analysis of Ir and Ru metals in the anode layer XPS		B.E. Ir $4f_{7/2}$	B.E. Ru $3p_{3/2}$	Mean particle size anode	Mean particle size cathode
Units	μm	Ir at. %	Ru at. %	Ir at. %	Ru at. %	eV	eV	nm	nm
FRESH MEA	90 ± 2	70.1 ± 0.5	29.9 ± 0.5	75.4 ± 2.0	24.6 ± 2.0	62.18	463.48	6 ± 2.0	2.5± 0.5
MEA operate in steady-state mode	81 ± 3	70.7± 0.5	29.3 ± 0.5	76.2 ± 2.0	23.8 ± 2.0	61.50	462.67	6 ± 2.0	3.0 ± 0.5
MEA operated with load and thermal cycles	84 ± 3	76.7± 0.5	23.3 ± 0.5	80.3 ± 2.0	19.7 ± 2.0	61.82	462.84	5 ± 2.0	3.5 ± 0.5

In a recent article [53], the main degradation mechanisms for proton exchange membrane electrolyzers have been reviewed. These mechanisms appear to be accelerated by specific stressors such as high current density, dynamic operation, and shutdown modes. Yet, most of the previous degradation studies, dealing with dynamic mode, have mainly regarded operation at current densities up to 1-2 A cm^{-2} and using MEAs containing high precious metal catalyst loadings (2-3 mg cm^{-2}). The main degradation mechanisms for these operating conditions are associated with anode catalyst dissolution, membrane chemical decomposition, and formation of semiconducting oxides on the metal components.

Rakousky et al have investigated PEM electrolysis cell operation up to 3 A cm^{-2} but using high catalyst loadings of 3 mg PGM cm^{-2} [24]. At elevated current densities, two primary factors have been identified to cause performance degradation, i.e. the increase in ohmic cell resistance and

the appearance of mass-transport resistance [24]. Both aspects appeared to contribute to the voltage increase in equal measure [24].

Of course, operation at higher currents in combination with much lower catalyst loadings, corresponding to significantly higher turnover frequencies [25], as in the present case, introduces new aspects, such as an increase of recoverable losses effects associated with catalyst modifications and mass transfer issues as well as an increase of irreversible degradation mainly affecting the anode catalyst.

The aim of this work was thus to understand if, under these specific conditions of high current density and low PGM loading, the dynamic operation could affect cell degradation in a much more relevant way compared to the continuous operation. This does not seem the case according to both the results of durability studies and post-operation analyses. Such evidences are in agreement with the literature reports for large catalyst loaded MEAs [22] showing that dynamic operation does not enhance significantly the degradation in the case of high PGM loadings and mild operating current densities. Even if, it has been observed that the dynamic mode may cause relevant membrane thinning [22]. In our case, we have evidence that the uptime hours at high current density are more relevant in determining membrane thinning than the dynamic operation. However, it is important to consider that this phenomenon is very much depending on the degree of stabilisation of the membrane consequent to its associated post-fluorination treatment.

In general, it appears that, although similar degradation mechanisms are identified for most of the investigated PEM electrolysis devices, the impact of each mechanism can vary according to the operating conditions, i.e. current density, operation mode (dynamic or continuous), catalyst loading, membrane thickness and stabilisation treatment, and type of cell configuration including porous transport layers, bipolar plates etc. Degradation can also vary significantly in different regions of the MEA according to the specific cell design [54].

Different operation strategies require specific analyses to identify the factors that can have the main influence in determining the life-time of a PEM electrolysis device.

Conclusions

The effects of high frequency and high current density (3 A cm^{-2}) load cycling, as well as thermal cycling, on the degradation of low metal catalyst loading-based MEAs (0.44 mg$_{PGM}$ cm^{-2}) have been here investigated. Previous literature reports have mainly dealt with understanding the degradation mechanisms of high precious metal loading-based MEAs operated under at moderate current densities. However, dynamic operation at high frequency and high current density for low catalyst loading MEAs is of relevant interest to decrease capital costs and to better understand the grid balancing service (grid stabilisation, peak shaving etc.) characteristics of next generation electrolysers. Electrolysis operation under such harsh conditions can in principle exacerbate MEA degradation thus decreasing the impact of the specific advantages.

It was observed that the smaller cell voltage increases for the low PGM loaded MEA operated continuously at high current density compared to the same MEA subjected to dynamic mode was essentially related to a larger decrease of series resistance during operation. This effect was associated to a larger membrane thinning during the steady-state mode compared to the cycled operation. Such phenomenon compensates for a larger increase of polarization resistance associated to mass transfer issues, at high current density, under continuous operation.

Accordingly, it is expected that, in the case of membranes properly stabilized to sustain operation at high currents without thinning effects, the cell voltage increase caused by load cycles would not be higher than that recorded during the steady-state operation. The main differences observed between these two different operating modes are that load cycling can exacerbate catalyst degradation while continuous operation causes larger recoverable losses and polymer electrolyte thinning. On the other hand, under some circumstances, load cycles can play a

temporary positive effect, at least in terms of catalyst regeneration and/or reduction of mass transfer issues at high current density (refresh cycles).

It appears that, in a durability study, keeping the cell at zero current for sufficient times can allow to recover part of the reversible losses. This aspect may involve two different phenomena, i.e., excursion at lower potentials could regenerate the catalyst by changing the oxidation state on the surface according to the different potential window and/or allowing the gas molecules entrapped in the micro-pores to escape from the catalyst layer. The latter phenomenon can reduce the gas supersaturation in the catalytic layer with a consequent gain in efficiency in the subsequent electrolysis step. The occurrence of a second semicircle in the low frequency range of the ac-impedance spectra obtained at high currents would corroborate the mass transfer issues mechanism. In fact, this semicircle is more evident under the conditions where recoverable losses occur at larger extent (steady-state operation). However, a partial recover of reversible losses is also observed during load cycling at high frequency that is more compatible with a change of the anode catalyst oxidation state. Possibly both mechanisms (escape of gases entrapped in the micropores and catalyst surface regeneration at low current densities) may occur during such current switches and appear beneficial for recovering voltage losses.

Beside recoverable losses, irreversible catalyst degradation is causing an increase of polarization resistance in the activation region for the used MEAs. This is slightly larger for the cycled MEA compared to the MEA operated in a steady-state test. Formation of substoichiometric IrRu-oxide on the surface of the used MEAs appears to be one of the main degradation factors accounting for irreversible catalyst degradation during operation at high current density beside the loss of Ru species especially observed after dynamic operation. The impact on catalyst degradation caused by the substoichiometric oxide phase occurrence at the anode surface, upon prolonged operation, appears slightly lower than the loss of Ru species. In fact, the increase of

polarization resistance in the activation region of the polarisation curve is slightly more relevant in the case of cycled operation where Ru losses are identified. Interestingly no relevant growth of the nanosized catalyst particles is observed.

The acquired knowledge may be helpful in designing more stable MEAs for operation under such harsh dynamic operating conditions by focusing on stabilised membranes, robust solid solutions of Ir and Ru oxides with tailored core-shell structures and enhanced morphologies for the catalyst layers.

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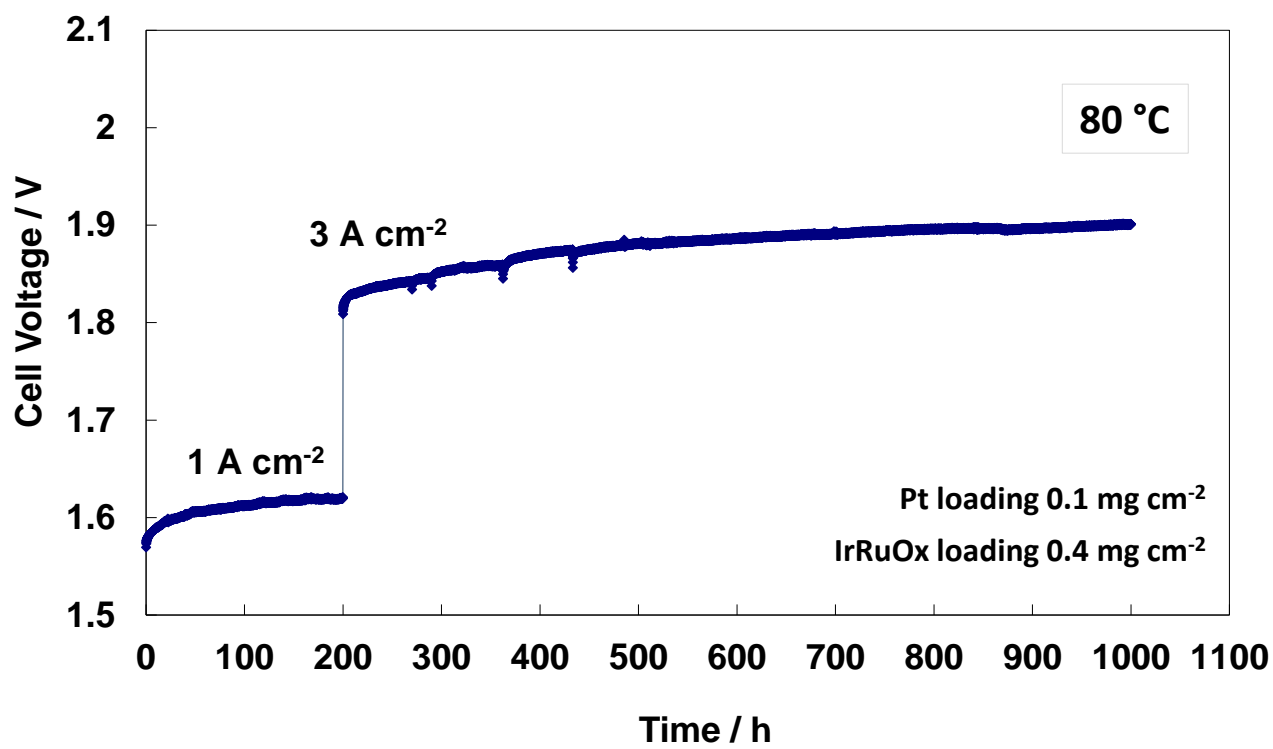
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Table1

Table 1. Survey of main results from ex-situ physicochemical analysis

	Membrane thickness	Bulk elemental analysis of Ir and Ru metals in the anode layer SEM-EDX		Surface elemental analysis of Ir and Ru metals in the anode layer XPS		B.E. Ir $4f_{7/2}$	B.E. Ru $3p_{3/2}$	Mean particle size anode	Mean particle size cathode
Units	μm	Ir at. %	Ru at. %	Ir at. %	Ru at. %	eV	eV	nm	nm
FRESH MEA	90 ± 2	70.1 ± 0.5	29.9 ± 0.5	75.4 ± 2.0	24.6 ± 2.0	62.18	463.48	6 ± 2.0	2.5± 0.5
MEA operate in steady-state mode	81 ± 3	70.7± 0.5	29.3 ± 0.5	76.2 ± 2.0	23.8 ± 2.0	61.50	462.67	6 ± 2.0	3.0 ± 0.5
MEA operated with load and thermal cycles	84 ± 3	76.7± 0.5	23.3 ± 0.5	80.3 ± 2.0	19.7 ± 2.0	61.82	462.84	5 ± 2.0	3.5 ± 0.5

Fig. 1 (a) Polarization curves at 80 °C and (b) ac-impedance spectra at 1.5 V and 1.8 V for the fresh

PEM electrolysis MEA

Fig. 2 MEA steady-state durability test at 1 and 3 A cm^{-2} and 80 °C

Fig 3 MEA current density (load) cycles at 80 °C; Pt loading: 0.1 mg·cm^{-2};
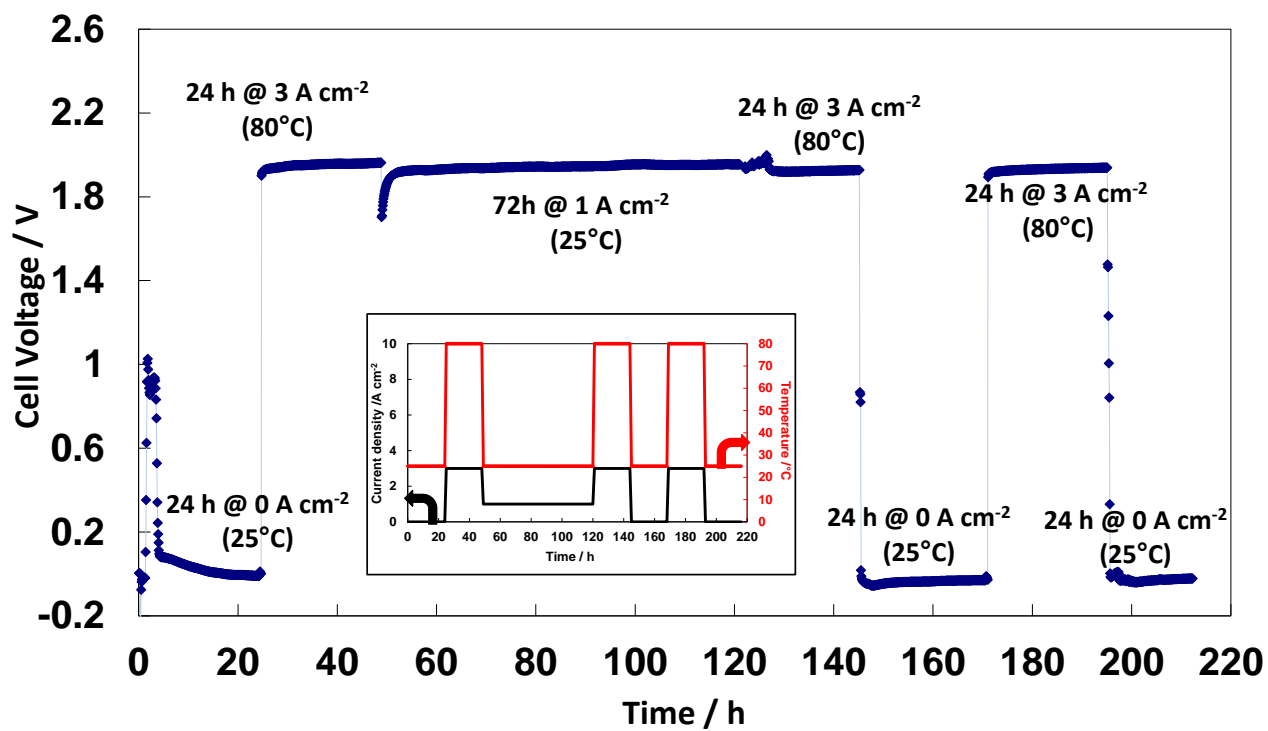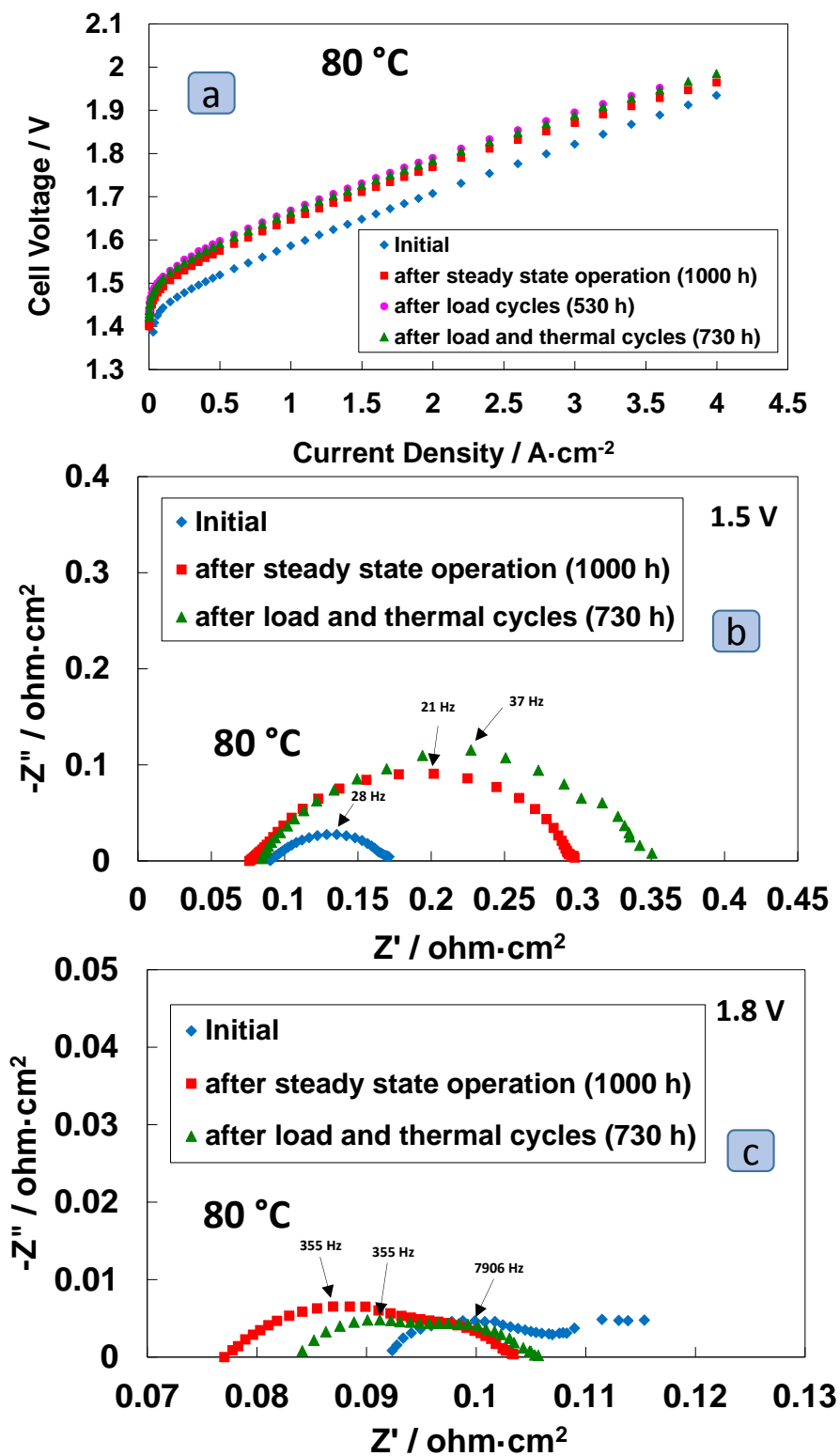
IrRuOx loading: 0.4 mg·cm^{-2}

Fig. 4 Temperature and current cycling of the PEM electrolysis MEA; the test protocol is shown in the inset; Pt loading: 0.1 mg cm^{-2}; IrRuOx loading: 0.4 mg cm^{-2}

Fig. 5 MEA polarization curves (a) and impedance spectroscopy at 1.5 V (b) and 1.8 V (c) before

and after steady-state durability and cycle tests; Pt loading: 0.1 mg·cm^{-2}; IrRuOx loading: 0.4
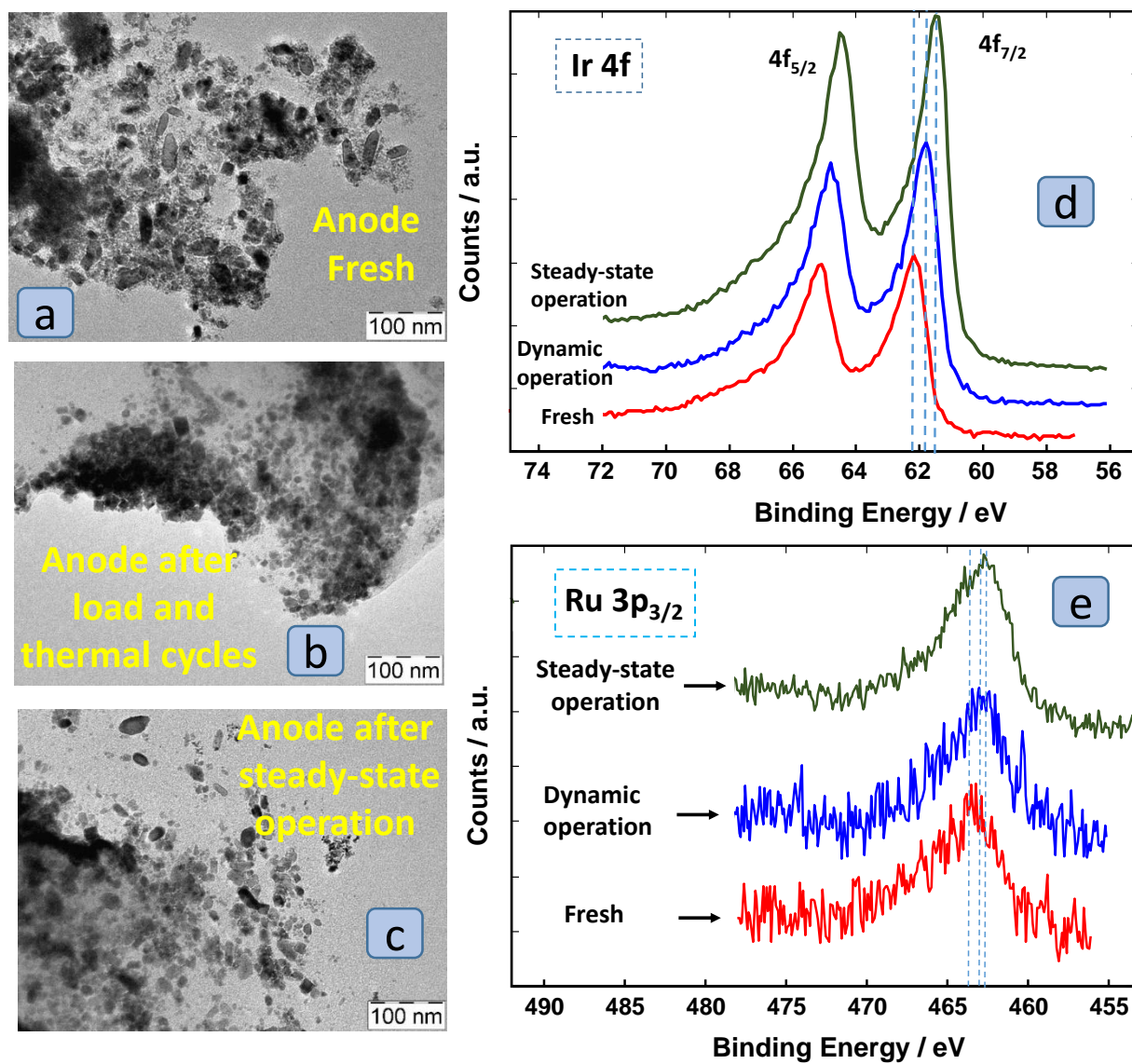
mg·cm^{-2}

Fig. 6 SEM Cross-sections of fresh (a) and used MEAs subjected (b) to combined 740 h load and thermal cycles (c) and to 1000 h steady-state electrolysis operation (the cathode layer is shown on the top for all MEAs)
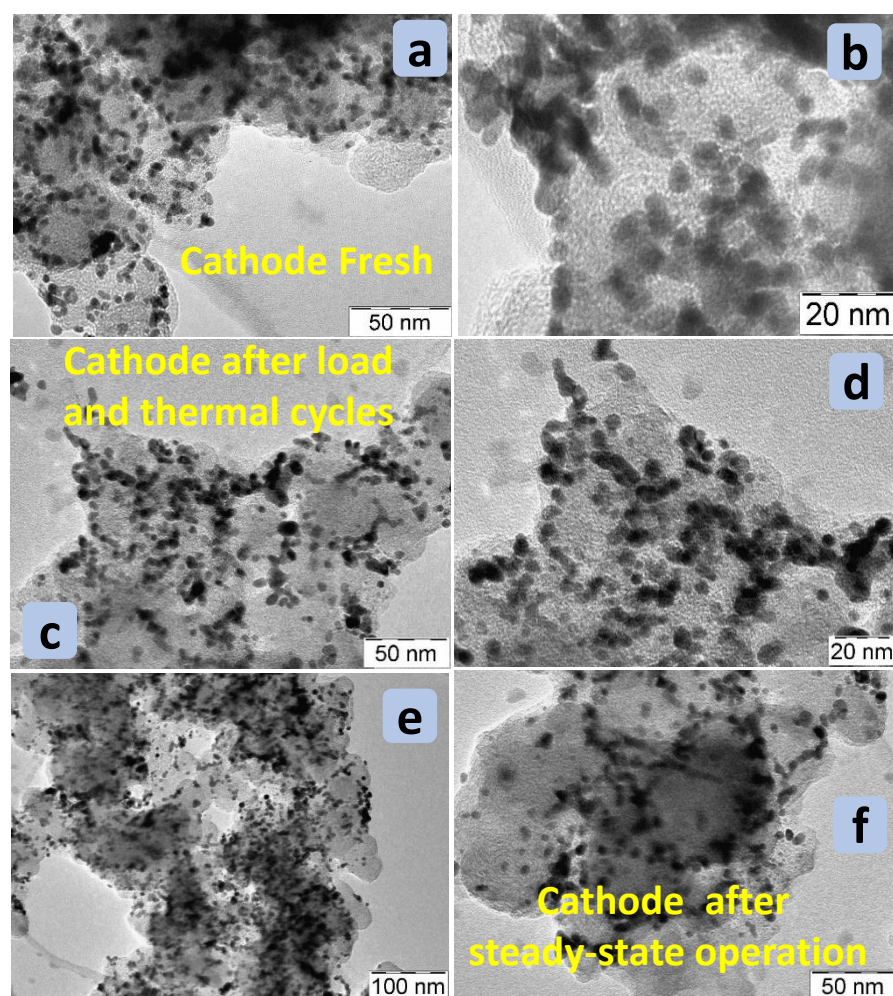
Fig. 7 TEM images for the fresh anode (a), the anode after 740 h load and thermal cycles (b), and the anode after 1000 h steady-state operation (c); high resolution Ir 4f (d) and Ru 3p$_{3/2}$ (e) XPS analyses before and after the 740 h combined electrolysis cycling tests (dynamic operation) and 1000 h steady-state operation.

Fig. 8 TEM images for the fresh MEA cathode (a-b), the MEA cathode after 740 h load and thermal cycles (c-d), and the MEA cathode after 1000 h steady-state durability test (e-f).

Supplementary Materials