

## Differential Resistance Analysis – Current Achievements and Applications

Z. Stoynov<sup>†</sup>, D. Vladikova<sup>\*</sup>, B. Burdin

Acad. E. Budevski Institute of Electrochemistry and Energy Systems- Bulgarian Academy of Sciences,  
10 Acad. G. Bonchev Str., Sofia 1113, Bulgaria

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Some of the most severe hurdles towards deployment of fuel cells are lifetime and durability. For Solid Oxide Fuel Cells (SOFCs) the degradation rates (DR) currently reported are below 1%  $\text{kh}^{-1}$ , with a tendency for further decrease to 0.1%  $\text{kh}^{-1}$ . The SoA degradation already requires long term testing, which takes several years. In addition to the accelerated stress tests, the testing time can be shortened by increasing the sensitivity and accuracy of the monitoring and diagnostic tools. This work presents a new method for degradation evaluation with higher sensitivity due to its operation with derivatives, named Differential Resistance Analysis (DRA). It applies the Differential Resistance  $R_d$  extracted from the current-voltage ( $i$ - $V$ ) characteristics and its time-evolution. The introduction of a spectral transformation procedure additionally increases the noise immunity and sensitivity of the method. The DRA works with two new performance indicators:  $R_{d,\min}$  and  $\Delta U^*$  which are more sensitive respectively to transport and to activation losses. A more detailed information illustrated with examples on SOFC about the methodology, the advantages in respect to sensibility and noise immunity, the possibilities to evaluate the state of health and to register early warning signals, is presented. The results show about 10 times higher sensitivity towards evaluation of the DR in comparison with the classical approach.

**Key words:** degradation rate, SOFC, current-voltage characteristics, differential resistance, spectral transform

### INTRODUCTION

Some of the most severe hurdles towards deployment of fuel cells (FC) are lifetime and durability, which still determine large part of the total costs. For evaluation of their operational stability on cell, stack, or system level, the parameter “degradation rate” (DR) is introduced. For its definition more often the decrease of the voltage for 1000 hours operation ( $\text{mV.kh}^{-1}$ ) at constant load is used after linearization of the voltage-time ( $V$ - $t$ ) dependence. It may be performed for the whole testing time, thus giving the average DR, or for segments defining degradation stages [1]. The voltage change may be replaced with that of the corresponding area specific resistance ( $\text{m}\Omega.\text{cm}^2.\text{kh}^{-1}$ ) [2-4]. For convenience the DR is expressed also in %.

For Solid Oxide Fuel Cells (SOFCs), which have flexibility towards the type of fuel [5], ability to tolerate the presence of impurities, higher efficiency combined with application of non-noble metal catalysts, the degradation rates currently reported are below 1%  $\text{kh}^{-1}$ , while the near future targets are for its further decrease to 0.1%  $\text{kh}^{-1}$  [6-8]. For Solid Oxide Electrolyzers

(SOEL) it exceeds 2 %  $\text{kh}^{-1}$  [1, 9].

For faster development and integration of new materials and architectures [10, 11, 12] and thus for increase of lifetime, it is important to understand and quantify the degradation and its mechanisms, to describe them with models validated and transformed into predictive performance tools for fast assessment of the different degradation sources, of their origin and interactions, of dominating aging factors. There are some successful results confirming the efficiency of this approach [1, 13-20]. However, the accumulation of reliable data requires long term testing, which takes several years. Obviously this is a serious barrier, because the needed testing time is not compatible with that requested for market deployment of the tested products.

The testing time may be decreased by introduction of accelerating tests and by increase of the testing sensitivity. The accelerating stress test (AST) procedures and protocols are well introduced in batteries testing. The application of this approach is more advanced in PEMFC, while in SOFC they are currently under development [21, 22]. ASTs have to shorten the testing time, however, activating the same ageing mechanisms as in non-accelerated testing. This is a critical moment in the procedure, since the measured degradation should be transferred to the real-world behavior of the

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To whom all correspondence should be sent:  
E-mail: d.vladikova@bas.bg

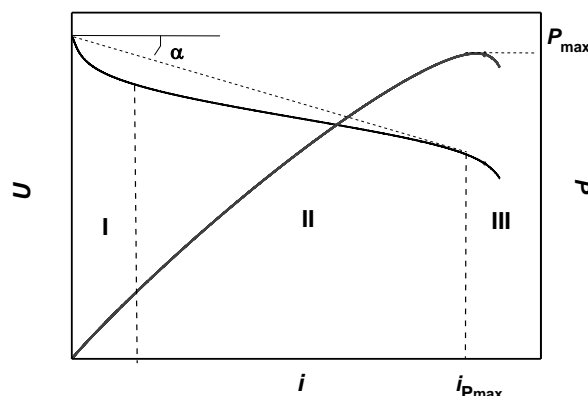
tested system. Thus the selection of the acceleration parameters and the level of acceleration are of critical importance and may differ a lot for different systems and applications. The risk of test „pre-acceleration“ can be decreased and the testing time shortened by increasing the sensitivity and accuracy of the monitoring and diagnostic tools and thus providing reliable quantitative information about the evolution of the system, which is the aim of the presented work. This approach should be compatible with both the existing test station hardware and the applied electrochemical testing procedures.

From system theory point of view, fuel cells, as electrochemical power sources, are nonlinear large statistical systems with multi-parametric conditioning. During long term testing in addition to the voltage-time dependences, periodically (on 500 - 1000 hours) current-voltage ( $i$ - $V$ ) characteristics are recorded for acquiring more informative outputs. They give integral picture of the system (cell, stack) for a given state, ensuring the simplest external general description of fuel cells ability to produce electrical energy. The  $i$ - $V$  curves describe the interrelation between the power components – voltage and current, which cover the entire operating region and reflect the dominant phenomena governing the process of electrical energy generation.

There are several important parameters of the  $i$ - $V$  curves which can be regarded as performance indicators of the generator: open circuit voltage (OCV) – the voltage at zero current; power characteristics - the derivative power-current ( $P$ - $i$ ) dependence which determines the maximum available power  $P_{\max}$ ; the corresponding internal resistance ( $R_i$ ) which has a minimum value ( $R_{i,\min}$ ) at that point and can be also recalculated as surface resistance, named area specific resistance (ASR). The vector of the parameters extracted from the  $i$ - $V$  curves which describes in the most general way the ability of a given power source to produce power is used for characterization of fuel cells during their design, optimization and operation analysis. It forms the kernel of the Performance Vector, which includes also the operation conditions.

The electrochemical processes generating the electrical energy take place at the triple phase boundaries in the porous electrodes structure. They are also tightly connected with the transport processes in the gas- and in the solid phases. As far as electrochemical reactions are in nature non-linear, in general the  $i$ - $V$  characteristics have also non-linear behavior. The typical  $i$ - $V$  shape has three regions (Fig. 1) – a non-linear quasi-exponential part at low currents (Region I), which reflects the

non-linear electrochemical reactions, followed by the quasi-linear Region II, dominated by linear (electron and ion) transport processes. At high currents the curve becomes again non-linear and steep (Region III), due to the concentration (mass transport) voltage drop caused by the fast consumption of the reactive gases [23, 24].



**Fig.1.** Current-voltage and current-power curves (schematic presentation).

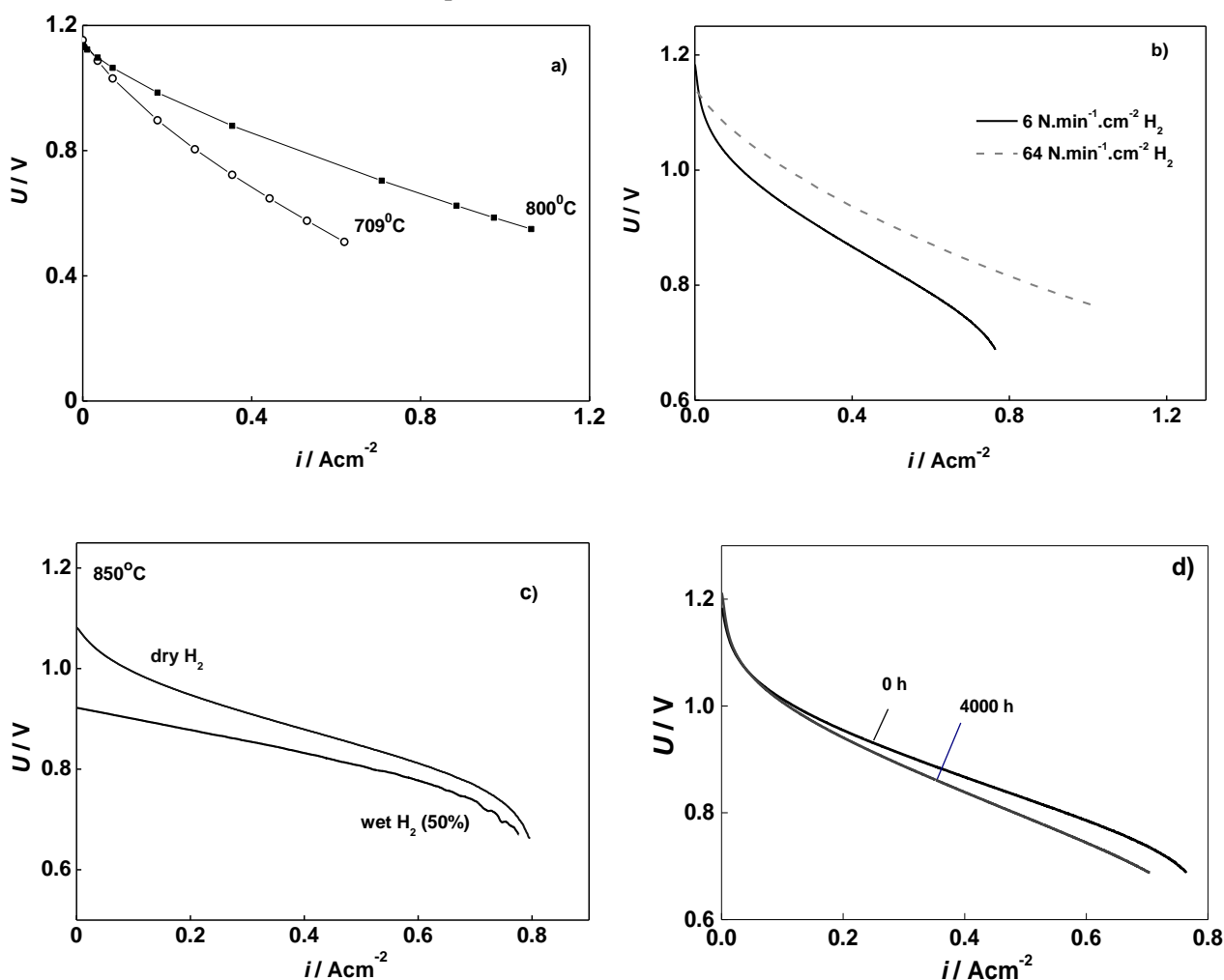
Since the external behavior represented by the  $i$ - $V$  curves is an integral product of a series of processes taking place in the constructive elements of the fuel cell and at their interfaces, it reflects all dominant phenomena governing the process of electrical energy generation and thus - the dominant barriers. However, the collection of more detailed information directly from the  $i$ - $V$  measurements is still not possible, but challenging. To answer the demand for extraction of more information from the volt-ampere characteristics in respect to diagnostic and degradation, a new method with higher sensitivity, named Differential Resistance Analysis (DRA) was recently developed [25]. It is based on the differential analysis of the volt-ampere characteristics (DIVA). The information can be enriched with impedance measurements in selected working points of the  $i$ - $V$  curves for deeper insight into the different degradation sources and improved understanding of ageing factors. The first publications on that topic aim to prove and evaluate the applicability of the method. This work is presenting more detailed information illustrated with examples on SOFC about the methodology, the advantages in respect to sensibility and noise immunity, the possibilities to evaluate the state of health (SoH) and to register early warning signals (EWOS), as well as requirements for collection of sufficient data with high quality. The experimental data are gathered from tests on button cells with dense YSZ electrolyte with thickness of about 5-10  $\mu\text{m}$  supported by a thick porous Ni-YSZ hydrogen electrode of 260  $\mu\text{m}$ . The oxygen electrode is a porous composite LSCF/CGO. A thin barrier layer

of CGO is deposited between the electrolyte and the LSCF electrode for limitation of the chemical reactivity. A pure LSC layer is used for current collector. The technology is a subject to proprietary information of SOLIDpower.

#### METHODOLOGY OF THE DIFFERENTIAL RESISTANCE ANALYSIS

To meet the challenge for sensitive degradation rate evaluation, a more detailed analysis of the current-voltage curves behavior and properties has been performed based on data from the literature, from producers catalogues, from own measurements and digital data from projects partners. The results confirm that  $i$ - $V$  characteristics are sensitive to conditioning parameters such as temperature, quality and quantity of fuel and oxidizer, humidity etc. (Fig. 2a-c). At constant operating conditions they are dependent on the degradation (Fig. 2d). The parametric changes reflect in variations of the curves shape. Thus at

constant operating conditions the deviations out of preliminary defined limits can serve as a measure for degradation. The quantitative estimation of the  $i$ - $V$  shape can be accepted as performance indicator. For convenience the different profiles are classified in several general groups based on resemblance with letters from the alphabet. The most general is the “s” type shape in which the three regions presented in Fig. 1 are observed. It may be modified in “j” type curve with linear slope in Region I (Fig. 2c for wet hydrogen). Since the load current corresponding to Region III is not appropriate for operation, often the  $i$ - $V$  curves include Regions I and II with the more typical “i” type curve (Fig. 2 a) and its “l” type modification with a quasi-constant slope. For more complicated structures, as double layered anodes or other types of structural or performance inhomogeneities more complicated shapes such as the “ss” one can be observed [26].



**Fig. 2.** Current-voltage curves at different operation conditions: a) different temperature; b) different quantity of fuel; c) wet and dry  $\text{H}_2$ ; d) at 0 h and 4000 h testing.

Shape Analysis

As it was already discussed the  $i$ - $V$  curves are representing the integral external response of a series of internally linked processes that take place in the different components of the SOFC - in the volume, or at the different interfaces. The main purpose of the numerous studies is to go deeper into the elementary steps and mechanisms of the electrochemical reactions and to learn how to optimize and govern them. However, taking into account the different nature and the big variety of those internally linked processes, the total deterministic description of their integral external behavior becomes impossible. The problem solving approach is to represent the  $i$ - $V$  characteristics as an external exhibition of the properties of a statistical and dynamically stochastic large system conditioned in definite operating environment. Those considerations suggest for application of statistical approaches for further analysis of the information coming from the  $i$ - $V$  curves. One effective approach is the Shape analysis based on the derivative parameter differential resistance  $R_d$ . The application of  $R_d$  has been suggested by some authors [2,4,6,13], but there is no registered progress in the literature.

The differential resistance can be obtained by differentiation of Ohm's law – i.e. as the derivative of the voltage  $V$  with respect to the current  $I$ :

$$R_{d,k} = dU_k/dI_k. \quad (1)$$

Calculated for every  $i$ - $V$  point, the values of  $R_d$  constitute a new function which describes the shape of the  $i$ - $V$  curve:

$$R_d = f(I). \quad (2)$$

The new “Shape analysis”, based on the analysis of  $R_d$  as a function of the current  $I$  (Eqn. 2), is named Differential Resistance Analysis (DRA).

In the general case the  $i$ - $V$  dependence and its corresponding derivative function are non-linear. As presented in Fig. 3a for “s” type curve, the differential resistance sharply decreases in the beginning, reaching a minimum and then increases again. Three characteristic regions can be separated: Region I, which is connected with the activation losses, Region II, which concerns the transport losses and Region III, where the gas diffusion limitations are dominating. As far as the  $i$ - $R_d$  dependence presents a derivative function, it offers additional new information which is coded in the  $i$ - $V$  curves. It is important to find characteristic

points of the  $i$ - $R_d$  dependence which can quantitatively describe the new functional dependence and can serve as additional performance indicators.

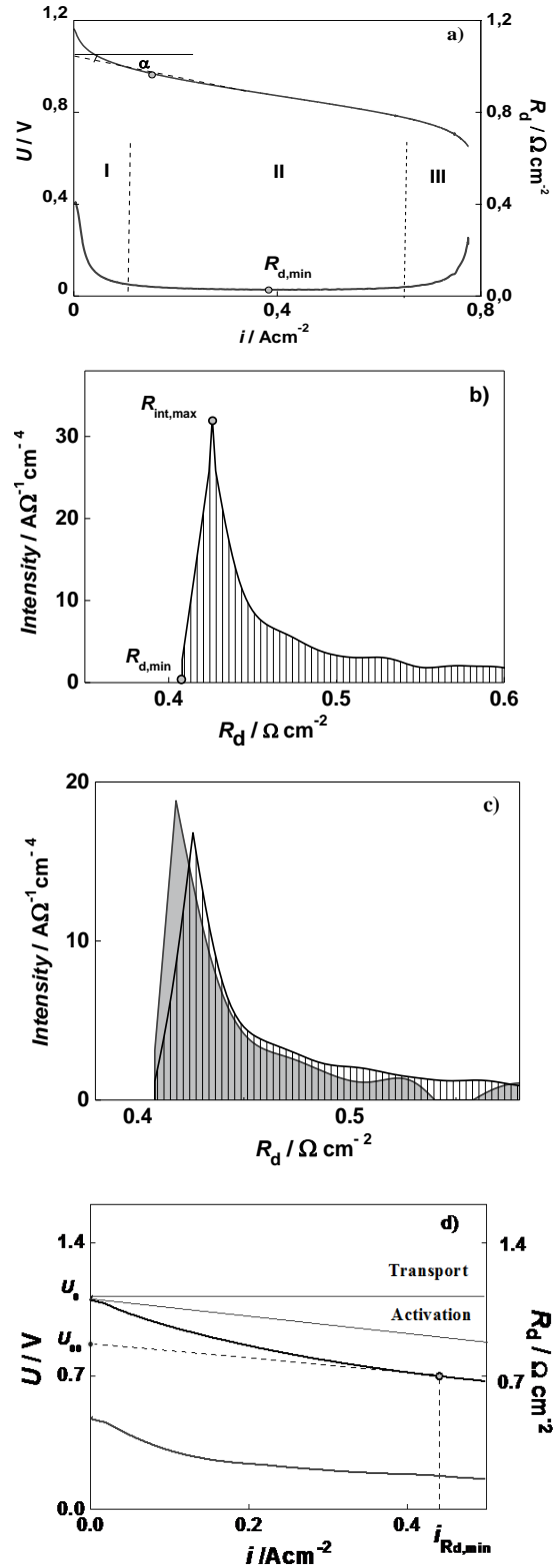


Fig 3. DRA procedure: a)  $i$ - $V$  curve and  $R_d/I$  dependence; b) spectral transform of the  $R_d/I$  dependence; c) twin spectra; d) determination of the performance indicator  $\Delta U^*$  (data from  $i$ - $V$  curve of button cell sample tested 1200 h).

The minimum of the differential resistance  $R_{d,\min}$  can be regarded as an important characteristic point for the cell performance. It reflects the state of health at constant operating conditions, since it is determined by the intrinsic properties of the system and not by the external conditions as the load current. In addition,  $R_{d,\min}$  is more sensitive to changes since it corresponds to the point where the derivative becomes zero. It should be noted that  $R_{d,\min}$  does not match  $R_{p,\max}$ . Impedance measurements could be important supporting information source.

### *Spectral Transform*

The  $R_d$ - $i$  curve can be presented in the more illustrative spectral form applying the Spectral Transform (ST) technique of aperiodic functions. It has been developed and applied for specialized analysis of impedance data, ensuring deeper observations based on enhanced sensibility, precision and noise immunity [27-29].

For DRA the ST converts the functional dependence (2) into the inverse one and produces the new functional dependence

$$dI/dR_d = F(R_d), \text{ i.e.} \quad (3)$$

$$S_{R_d} = \text{ST}[F(R_d)]. \quad (4)$$

Thus the ST procedure converts the horizontal parts of the  $R_d/I$  plot into spectral picks with definite intensity (Fig. 3b). Since the parametric  $R_d$  spectrum is obtained by accumulating current regions with approximately equal values of this parameter, the intensity of the individual spectral peak is proportional to the length of the current range with similar values of the differential resistance.

In principle the spectral transform is not simply a presentation of the same data in different coordinates. By its nature it is a type of regression analysis which filters the statistical noises coming from the object itself and from the performed measurements, as well as non-statistical noises. Its high power of filtration is eliminating the possible wild points and the resulting “black” noise, since the presence of an outlier introduces a fuzzy low intensity line, located away from the spectral kernel of the assembly representing the basic phenomenon. The spectral peaks also provide objective information about the degree of dispersion, which is unavailable by other methods

for analysis. The width of every spectral peak increases with the enhancement of the dispersion.

The produced Differential resistance spectrum of the “s” shaped  $i$ - $V$  curve has two specific areas of interest – the spectral peak in the vicinity of  $R_{d,\min}$  which presents Segment II from Fig. 3a and the long tail corresponding to segments I and III. The spectral maximum has 2 characteristic points:  $R_{d,\min}$  - the minimum value of the differential resistance and  $R_{\text{int,max}}$  – the value of the spectral maximum, which gives the most stable value of  $R_d$  observed in the widest current region. The spectral tail is produced by accumulation of similar  $R_d$  values, however coming from Segments I and II and thus with different origin in respect to the internal processes. To avoid the ambiguity, they can be separated as “twin spectra” describing the spectral behavior before and after  $R_{d,\min}$  (Fig. 3c).

Although reflecting the general internal behavior of the system, being situated in Segment II,  $R_{d,\min}$  is expected to be more sensitive to transport limitations. It is useful to find performance indicator with higher sensitivity towards activation losses. The DRA determines the value of  $R_{d,\min}$  and the corresponding current in the  $i$ - $V$  curve (Fig. 2d). The tangential in this point ( $I_{R_{d,\min}}$ ) defines the voltage  $U_{00}$  which is the voltage at  $I = 0$  in case the system would work with resistance equal to  $R_{d,\min}$ . The difference  $\Delta U^* = U_0 - U_{00}$  serves as a new indicator. Although connected with the position of  $R_{d,\min}$ , it is more sensitive to activation losses.

The  $i$ - $V$  shape analysis performed by the DRA introduces two additional performance indicators:  $R_{d,\min}$  and  $\Delta U^*$ . Each of them has higher selectivity in respect to different degradation sources:  $\Delta U^*$  is more sensitive to activation losses and  $R_{d,\min}$  - to transport hindrances which is a step forward towards identification of the degradation sources. A combined usage of the derived indicators is recommended since they may be sensitive to different degradation processes and sources. Additional impedance measurements can give more precise information about the origin of the degradation.

### *Applications and Specific Requirements*

The DRA has very high sensibility towards degradation, since it works with the derivatives of the measured parameters, which are in principle more sensitive to small deviations. This is an opportunity for collection of reliable data from shorter tests avoiding severe accelerating conditions. Fig. 4 presents results from durability tests on button cell carried out for 1200 hours. For

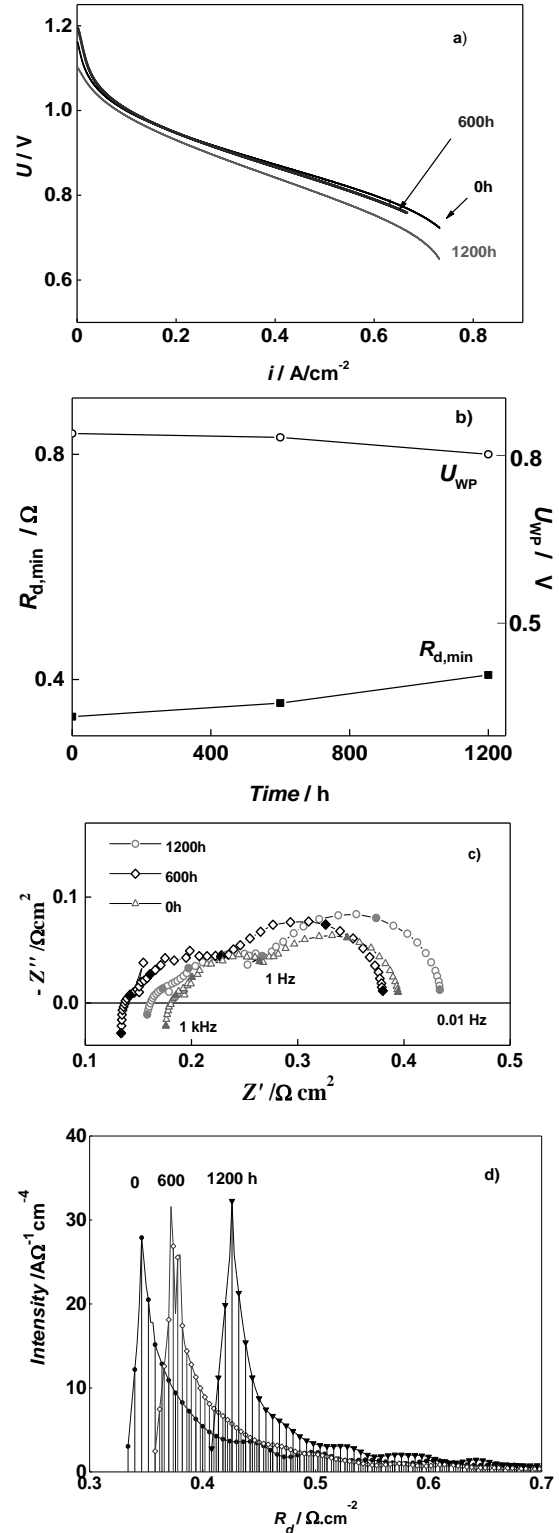
the first 600 hours there is no significant difference in the  $i$ - $V$  curves (Fig. 4a). The change of the voltage in the working point ( $U_{WP}$ ) at current load  $0.5 \text{ A/cm}^2$  is less than 10 mV (Fig. 4b, Table 1), i.e. the accuracy of the measurements is low. The registered change corresponds to linearized DR about  $1\% \cdot \text{kh}^{-1}$ . For reliable data longer testing is needed. The more detailed impedance characterization [30] shows temporal decrease of the ohmic resistance, very probably due to improved contacts (Fig. 4c). Obviously during the first 600 hours it compensates the progressive increase of the low frequency polarization resistance which is already dominating at  $1200^\circ\text{C}$ .

**Table 1.**  $R_{d,\min}$  and calculated degradation rate from initial  $i$ - $V$  curves measured on button cell tested for 1200 hours.

Time [h]	0	600	1200
$U$ at $I=0.5 \text{ A/cm}^2$ [mV]	837	830	800
$R_{d,\min}$ [ $\text{m}\Omega \cdot \text{cm}^{-2}$ ]	334	365	408
$R_d$ at $I=0.5 \text{ A/cm}^2$ [ $\text{A} \cdot \text{cm}^{-2}$ ]	435	420	360
$DR_U$ [ $\text{mV} \cdot \text{kh}^{-1}$ ]	-	12	31
$DR_U$ [ $\% \cdot \text{kh}^{-1}$ ]	-	1.3	3.7
$DR_{R_{d,\min}}$ [ $\text{m}\Omega \cdot \text{kh}^{-1}$ ]	-	52	61.6
$DR_{R_{d,\min}}$ [ $\% \cdot \text{kh}^{-1}$ ]	-	15.4	18.5

The evaluation of the DRA degradation is based on the time-dependence of the new performance indicator  $R_{d,\min}$ . Both  $R_{d,\min}$  and  $R_{\text{int,max}}$  change noticeably – about 7% (Fig. 4d) which corresponds to DR about  $15\% \cdot \text{kh}^{-1}$  (Table 1), i.e. the “zooming” effect of the DRA is about 10 times. For 1200 hours the degradation rate increases about 3 times, keeping the high “zooming” effect of the DRA (Table 1).

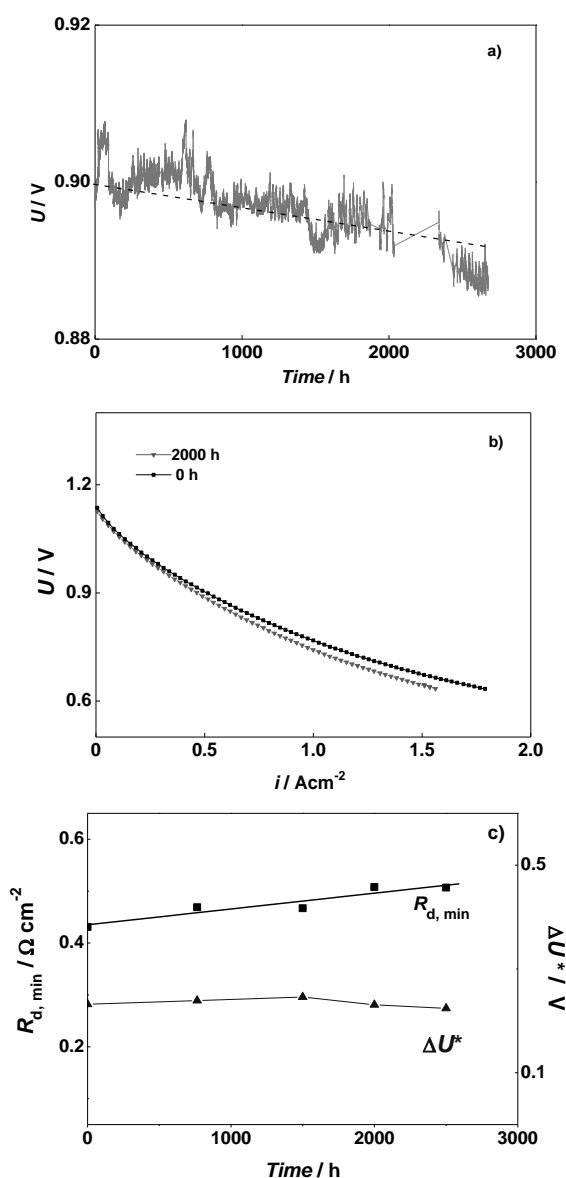
As it can be seen in Table 1, the testing current load ( $0,5 \text{ A/cm}^2$ ) is closer to that corresponding to  $R_{d,\min}$  of the pristine sample. However, with the increase of the degradation  $R_{d,\min}$  increases, while the corresponding current decreases, thus increasing the difference in respect to the testing load current. It is interesting to check if that increasing difference has accelerating effect in respect to degradation. Dedicated experiments for elucidating this hypothesis are under preparation.



**Fig. 4.** DRA of button cell tested 1200 hours: a)  $i$ - $V$  curves at 0; 600 and 1200 h; b) time dependence of  $R_{d,\min}$  and  $U_{WP}$ ; c) impedance diagrams at  $I = 0.5 \text{ A/cm}^2$ ; d) corresponding DRA spectra. Operating conditions:  $850^\circ\text{C}$ ;  $\text{O}_2$  flow =  $55 \text{ Nml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ ;  $\text{H}_2$  flow =  $6 \text{ Nml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ .

The next example of DRA application is on button cell tested 2600 hours. The analysis is based on the time dependence of  $R_{d,\min}$  and  $\Delta U^*$  as

performance indicators. The classical approach for calculation of DR, based on the operating voltage-time curve gives a very low value - below  $0,4 \text{ \%} \cdot \text{kh}^{-1}$  with low accuracy of the measurement (Fig. 5a). For higher data quality longer testing time is needed. As it can be seen in Fig. 5b, the  $i$ - $V$  curves are also quite similar. The most pronounced changes during testing are registered for  $R_{d,\min}$  (Fig. 5c). The DR evaluated by the change of this parameter is  $8\% \cdot \text{kh}^{-1}$  which is again an evidence for the high sensitivity of the DRA approach. The variation of  $\Delta U^*$  is small. This result can be explained with low activation losses. For this testing interval they are not the rate limiting factor for degradation.



**Fig.5.** DRA of button cell tested 2600 hours: a) time dependence of  $U_{wp}$ ; b)  $i$ - $V$  curves at 0 and 2000 h; c) time dependence of  $R_{d,\min}$ ,  $\Delta U^*$ ; Operating conditions:  $750^\circ\text{C}$ ; air =  $150 \text{ Nml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ ;  $\text{H}_2 = 64 \text{ Nml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ .

## FURTHER APPLICATIONS OF THE DIFFERENTIAL RESISTANCE ANALYSIS

The presented examples for application of the DRA in degradation evaluation and monitoring confirm the high sensitivity of the new approach which comes from the operation with derivatives. As far as every differentiation increases data noise, the diagnostic success requires acquisition of more precise and confident initial data coming from the  $i$ - $V$  measurements.

### Data Quality Requirements

The current-voltage measurements in SOFC follow a step-wise increase of the current up to a given limit and a step-wise decrease back to zero current [31]. Thus the  $i$ - $V$  measurements consist of a number of steps, i.e. of mini-cycles. Every mini-cycle should have a selected duration (hold time) with two periods - delay time and data acquisition time. The delay time is necessary (un-avoidable) for attaining a stable steady state of the object, since every change of the current to a new fixed value is followed by a relaxation period of the voltage, during which processes with different time-constants take place in the components of the cell. They are dependent on the cell/stack properties determined by various factors: selected materials, architecture, technology, external conditioning, state of the tested system etc. The relaxation ensures a stationary state needed for precise measurements, realized by the delay time before the measurement. After the end of the delay time starts the acquisition time, during which measurements of valid stationary data are carried out. The simplest way is to measure a single vector of data (time, voltage and current), however measurements of a set of data during the acquisition time provide for enhanced selectivity, precision and post-experimental assessment in respect to steady state and confidence. The full algorithm for a precise  $i$ - $V$  measurement for application of the DRA can be found in [32]. One  $i$ - $V$  curve measured for DRA performance should not exceed 40 measurement points.

### Early warning Output Signals

The production of high quality data from the  $i$ - $V$  measurements is a pre-requisite for the development of Early Warning Output Signals (EWOS) which is one of the most challenging targets in respect to SOFC monitoring and diagnostics since it paves the way towards development of urgent mitigation strategies during operation. The Warning Output Signals (WOS) practice is largely used in other technical zones

(machineries, buildings etc.). In the field of SOFCs, however, the accepted up to now approach of life testing applies simple measurements of the voltage at a constant current during operation at regular conditioning which cannot be effectively used for early diagnostic. An advanced approach is the periodic application of additional active input signals ( $i$ - $V$  curves or impedance) for acquiring more informative outputs, necessary for diagnostic purposes.

The development of the Differential Resistance Analysis provides for the introduction of EWOS technique for SOFC. The differential resistance is a derivative function. The defined value of  $R_{d,min}$  corresponds to the zero point of the  $R_d$  derivative – i.e. it is a second derivative. As a result, the changes of  $R_{d,min}$  are observable much earlier than the changes of the other parameters. Thus the  $R_{d,min}$  nature defines its properties to be used for early recognition of degradation, or other warning changes in the internal performance of the FC and thus for adequate diagnostic. The requirements for high quality initial data are mandatory.

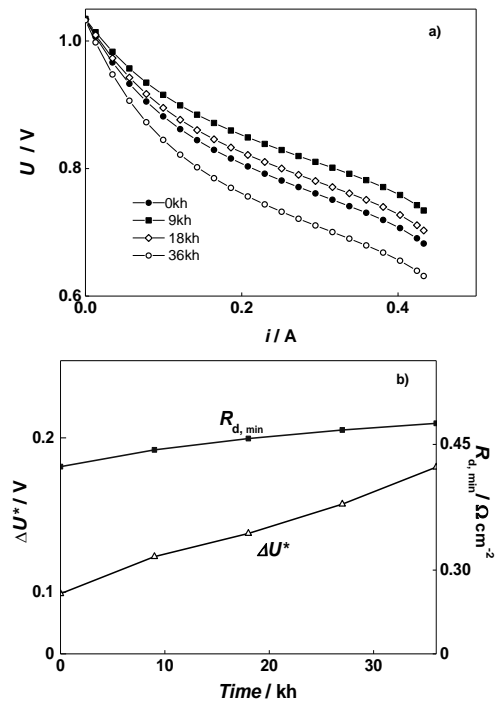
The simplest EWOS procedure comprises:

- Precise measurements of the  $i$ - $V$  characteristics (up to a preliminary defined current limit);
- Differential Resistance Analysis – calculation of  $R_d$ , Spectral Transform, determination of  $R_{d,min}$  and  $\Delta U^*$ ;
- Consecutive performance of these two steps during life testing according to selected consequence of measurements;
- Calculation and monitoring of the DR, or the relative deviations of  $R_{d,min}$  and  $\Delta U^*$  in respect to its values in the pristine cell.

Since the DRA indicators are more sensitive, the early notification of sharper deviations from their smooth change can serve as EWOS for increased degradation, or another deterioration. Every indicator has higher selectivity in respect to different degradation source ( $\Delta U^*$  is more sensitive to activation losses and  $R_{d,min}$  - to transport hindrances). The application of additional indicators and impedance measurements can give more precise information about the origin of the degradation (ohmic losses, electrodes polarization etc.) [33].

DRA was performed on simulated  $i$ - $V$  curves of a cell in a large stack operated for 36000 hours. The degradation affects the electrolyte, the anode (Ni-YSZ) and the cathode (LSM-YSZ). Cr contamination of LSM-YSZ causes the blocking of active sites. Thus the modeling conditions ensure high quality data (no external noise), constant operating conditions and constant degradation process reflecting both the activation and transport

processes, with special accent on the blocking of the cathode active sites. The performed DRA operates with  $R_{d,min}$  and  $\Delta U^*$ . The ageing affects smoothly both  $R_{d,min}$  and  $\Delta U^*$ . It is more pronounced in  $\Delta U^*$  (Fig. 6a,b). Thus the DRA confirms that the long term performance affects both the transport and the activation losses with stronger influence on the activation losses. The smooth linear increase of  $R_{d,min}$  and  $\Delta U^*$  indicates similar degradation which is introduced in the model and correctly captured by the DRA which guarantees an accurate description of the performance behavior reflecting the internal state of the system. It is expected that in case of degradation acceleration, this smooth dependence will be corrupted and the change will be observed earlier in respect to other indicators. For its experimental confirmation new modeling conditions will be introduced.



**Fig.6.** DRA of a cell in a large stack operated for 36000 hours: a)  $i$ - $V$  curves at 0, 9, 18 and 36 kh; b) time dependence of  $R_{d,min}$  and  $\Delta U^*$ .

## CONCLUSIONS

The development and approbation of the Differential Resistance Analysis technique based on the measured  $i$ - $V$  curves (DiVA) shows that it can be applied as a useful tool with increased sensibility and accuracy for diagnostics and monitoring of SOFC (cells/stacks) and quantitative evaluation of the degradation rate. It operates with new and more selective performance indicators ( $R_{d,min}$  and  $\Delta U^*$ ) which are extracted from the  $i$ - $V$  curves and ensure



collection of reliable data from shorter tests avoiding severe accelerating test conditions.

However, since the high sensitivity of the new approach comes from the operation with derivatives which *a priori* increase the data noise, the diagnostics success requires acquisition of more precise measurements that ensure high quality initial data with limited number – up to 40 points on *i-V* curve.

Further development of the method is planned for its broader application, which can exceed the SOFC niche. Since the generally accepted parameter for evaluation of the degradation rate is based on the change of the potential at constant current load with the time, it will be useful if a correlation with the DRA performance indicators is found. An important direction for further development of the DRA is its application for detection of early warning output signals.

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## Диференциален анализ на съпротивлението - постижения и приложения

З. Стойнов<sup>†</sup>, Д. Владикова\*, Б. Бурдин

Институт по електрохимия и енергийни системи „Акад. Евгени Будевски“, Българска академия на науките, ул. Акад. Г. Бончев, бл.10, София 1113, България

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(Резюме)

Най-големите препятствия пред внедряването на горивните клетки са времето на експлоатация и издръжливостта им. При твърдооксидните горивни клетки (ТОКГ) цитираните в литературата стойности за скоростта на деградация (СД) са под 1% кчас<sup>-1</sup>, с тенденция за по-нататъшно намаляване до 0,1% кчас<sup>-1</sup>. При такива стойности, за изследване на деградационните процеси, са необходими дълготрайни тестове с продължителност няколко години. Освен чрез ускорените стрес-тестове, времето за изпитване би могло да бъде съкратено и чрез увеличаване на чувствителността и точността на инструменталните подходи за мониторинг и диагностика. Настоящата работа представя новия метод Диференциален анализ на съпротивлението (ДАС) за оценка на деградацията. Той осигурява повишена чувствителност, оперирайки с производната диференциално съпротивление  $R_d$ , което се изчислява от волт-амперните ( $i-V$ ) характеристики и с неговата еволюция с времето. Въвеждането на процедурата на спектрална трансформация допълнително увеличава шумоустойчивостта и чувствителността на метода. ДАС работи с два нови характеристични за деградацията индикатора:  $R_d$  (минималното диференциално съпротивление) и  $\Delta U^*$ , които са по-чувствителни съответно към активационните и към транспортните загуби. В работата е представена по-подробна информация, илюстрирана с примери върху ТОКГ, които илюстрират методологията, предимствата по отношение на чувствителността и шумоустойчивостта, възможностите за оценка на състоянието и здраве и регистриране на ранни предупредителни сигнали за засилена деградация. Резултатите показват около 10 пъти по-висока чувствителност по-отношение на оценката на СД в сравнение с класическия подход.