JRC VALIDATED METHODS, REFERENCE METHODS AND MEASUREMENTS REPORT

EU harmonised cyclic voltammetry test method for low-temperature water electrolysis single cells

Malkow, T., De Marco, G., Tsotridis, G.

2018

EUR 29285 EN

Contact information
Name: T. MALKOW
Address: Westerduinweg 3, 1755 LE Petten, The Netherlands
Email: Thomas.Malkow@ec.europa.eu
Tel.: +31 226 56 5656

JRC Science Hub
https://ec.europa.eu/jrc

JRC111151

EUR 29285 EN

Print	ISBN 978-92-79-89870-9	ISSN 1018-5593	doi: 10.2760/140687
PDF	ISBN 978-92-79-89871-6	ISSN 1831-9424	doi: 10.2760/442574

Luxembourg: Publications Office of the European Union, 2018

How to cite this report: T Malkow, G De Marco, G Tsotridis, *EU harmonised cyclic voltammetry test method for low-temperature water electrolysis single cells*, EUR 29285 EN, Publications Office of the European Union, Luxembourg, 2018, ISBN 978-92-79-89870-9, doi 10.2760/140687, PUBSY No. 111151

Printed in *The Netherlands*

EU harmonised cyclic voltammetry test method for low-temperature water electrolysis single cells

Malkow, T., De Marco, G., Tsotridis, G.

THIS PAGE IS LEFT BLANK INTENTIONALLY

Contents

THIS PAGE IS LEFT BLANK INTENTIONALLY

Foreword

This report was carried out under the Framework Contract between the Joint Research Centre (JRC) and the Fuel Cells and Hydrogen second Joint Undertaking (FCH2JU) implemented by annual Rolling Plans.

According to the Rolling Plan 2018, this report was prepared under this contract as the part on "Testing procedures" of deliverable B.2.3 "Harmonised Electrolysis Testing".

THIS PAGE IS LEFT BLANK INTENTIONALLY

Acknowledgements

We would like to express our sincere gratitude to all participants and their respective organisations for their contributions in developing the EU harmonised cyclic voltammetry test method for low-temperature water electrolysis single cells document.

We would also like to thank the “Fuel Cell and Hydrogen second Joint Undertaking” (FCH2JU) Programme Office for the continuous support and encouragement we received throughout the preparatory stages of this report. FCH2JU is also thanked for its financial contribution.

THIS PAGE IS LEFT BLANK INTENTIONALLY

List of contributors

(in alphabetical order of their organisations and names)

AREVA H_2Gen	Fabien Auprêtre
Deutsches Zentrum für Luft- und Raumfahrt e. V.	Regine Reißner
Energy Research Centre of Netherlands	Frans van Berkel
Swiss Federal Laboratories for Materials Science and Technology	Ulrich Vogt
Institut de Chimie Moléculaire et des Matériaux d'Orsay – Université Paris-Sud	Pierre Millet
Istituto di Tecnologie Avanzate per L'Energia "Nicola Giordano"	Antonino S. Aricó

THIS PAGE IS LEFT BLANK INTENTIONALLY

1 Introduction

Cyclic voltammetry (CV) is a widely used *in-situ* electroanalytical characterisation technique for studying electrochemical redox reactions in electrochemical cells as they provide information on the steps involved in electrochemical processes (i.e. redox transitions, adsorption/desorption, double layer charging/discharging) with modest efforts in data acquisition and interpretation [1]. It is commonly used in the development of electro-catalysts as a screening tool to evaluate catalytic activity.

In CV, the potential of the low temperature water electrolysis (LTWE) cell is linearly swept at a constant scan rate ν from the start potential, $E_{initial}$ to the end potential, E_{final} to be reversed to the start potential creating a symmetrical triangular potential waveform while recording the Faradaic (i.e. by redox surface reaction) and capacitive (double layer charging of the electrode-electrolyte interface) current response known as cyclic voltammogram (profile of current or current response versus potential).

For repeated cycles, $E_{initial}$ and E_{final} are respectively replaced by the first vertex (switching) potential, E_{vert1} and the second vertex (switching) potential, E_{vert2} when different.

The potential sweep may be repeated as many times as needed. Where no charge transfer takes place at the working electrode (WE), only a capacitive current is recorded.

Usually, the current is small so that the voltage loss due to ohmic resistances also known as IR voltage drop is negligible depending on the sweep rate of the potential typically of between 5 mV/s and 200 mV/s.

However, for LTWE cells with high currents or high resistance, correction for IR voltage drop is advised.

This potentio-dynamic technique is usually applied in half-cell testing to eliminate possible interference from other reactions and is conducted in a three measurement electrode configuration comprising of WE which is the electrode of interest, counter electrode (CE) that enables the current flow and a reference electrode (RE) against which the WE potential is measured.

However, there is a specific interest for *in–situ* determination of the electrochemically active surface area (ECSA) of the electrodes in Polymer Electrolyte Membrane Water Electrolyser by using CV. It allows to *in-situ* study the catalyst utilisation and to investigate the ionomer-catalyst interface when different ionomers are used.

Some procedures used in the research community are given in Sec. 6 for proton exchange membrane water electrolysis (PEMWE) cell with Pt/C catalyst for the hydrogen evolution reaction (HER) at the cathode (under conventional PEMWE operation) and IrO_2 (respectively IrRu oxide) as oxygen evolution reaction (OER) at the anode.

The information obtained from CV measurements of a catalyst in LTWE single cells, measured from the hydrogen adsorption/desorption onto a metal catalyst (e.g. Pt) surface (each atom on the metal surface chemisorbs a single hydrogen atom), is the ECSA of the electro-catalyst. The catalyst utilisation, U_M (%) is the ratio of the ECSA (from CV) to the total specific surface area of the catalyst, A_{total} (m^2/g). It is generally a non-dimensional number reflecting the extension of the catalyst-electrolyte interface,

$$\mathrm{U_M} = \frac{\mathrm{ECSA}}{\mathrm{A_{total}}} \cdot 100\%; \qquad (1)$$

A_{total} is determined by physico-chemical methods. For an unsupported catalyst, A_{total} is usually determined by Brunauer–Emmett–Teller (BET) measurement [2] using nitrogen adsorption/desorption at the liquid nitrogen temperature.

For a supported catalyst such as Pt/C or Pd/C, A_{total} is determined from the mean particle size and the mass density of the metal [3].

Generally, a spherical shape of the nano-sized metal particle is assumed. The metal surface area (MSA) (m^2/g) is

$$\mathrm{A}_M = \frac{6 \cdot 10^4}{\rho \cdot d} \qquad (2)$$

where ρ (g/cm^3) is the density and d (Å) is the average size of the metal catalyst particle.

The mean particle size is either derived from transmission electron microscopy (TEM) or the broadening of the X-ray diffraction (XRD) peaks (Debye-Scherrer method) [4].

2 Objective and scope

This procedure is a general characterisation method that is used in research and development of the LTWE single cells. It addresses to the user as an experimenter performing on LTWE single cells measurements including data analysis of CV by measuring the Coulomb charge (integration of current with time) associated with the deposition or removal of a chemisorbed monolayer of electro-active species to determine the ECSA of the electro-catalysts in the electrode.

The user should refer to the scientific literature including the references cited herein for additional, more in-depth analysis including data post processing.

THIS PAGE IS LEFT BLANK INTENTIONALLY

3 Terminology, definitions and symbols

3.1 Terminology and definitions

Potentiostat/Galvanostat:

A potentiostat/galvanostat is the electronic hardware required to control a two, three or four electrode (namely: WE and CE, RE/Sense 1 and RE/Sense 2) configuration in an experiment. A potentiostat is to control the WE potential constant with respect to the RE by adjusting the current at an auxiliary electrode. A galvanostat maintains the current through the cell constant.

Sensor:

A sensor is a device that measures a physical quantity and converts it into a signal which is transferred to a data acquisition system. Each sensor (including the complete measurement chain) has a specific measurement uncertainty.

Electrolysis test stand:

An electrolysis test stand consists of a set of sensors, actuators, controls loops, piping, data acquisition systems etc. that allows operating and testing a single cell.

Measurement electrode:

A measurement electrode is an electrical conductor used to make contact between the LTWE cell and the potentiostat/galvanostat; those connections are done through (shielded) cables.

More extensive terminology definitions can be found in [5].

3.2 Symbols

The symbols used in this document are defined in Table 1.

Table 1 Definition of symbols

Symbol	Description (unit)
A	Geometric active area of the single cell (cm^2_{geo})
A_M	Metal surface area of the catalyst (m^2_{real}/g)
A_{total}	Total specific surface area of the catalyst (m^2_{real}/g)

Symbol	**Description (unit)**
CE	Counter or auxiliary Electrode (-)
DHE	Dynamic Hydrogen Electrode (-)
ECSA	Electrochemically active surface area (cm^2_{real})
sECSA	Specific ECSA (m^2_{real}/g)
E	Sweep potential (V)
E_1	Lower integration limit of the potential regarding Q_H calculation (V)
E_2	Upper integration limit of the potential regarding Q_H calculation (V)
$E_{initial}$	Start potential (V)
E_{final}	End potential (V)
E_{vert1}	First vertex potential of the potential sweep (V)
E_{vert2}	Second vertex potential of the potential sweep (V)
H_{ad}	Adsorbed hydrogen species (-)
I	Charging/discharging current (A)
j	Charging/discharging current density (A/cm^2)
M	Fraction of metallic catalyst surface (-)
n_{SEG}	Number of sweep potential voltammetry cycle segments (-)
q^*	Voltammetric surface charge
Q_{CS}	Feed flow rate through counter side of cell geometric area ($ml/min/cm^2_{geo}$)
Q_{SS}	Feed flow rate through studied side of cell geometric area [$ml/min/cm^2_{geo}$)
Q_H	Electric hydrogen desorption charge (-)
Q_{HO}	Electric hydrogen charge per unit area for full coverage of one mono layer of hydrogen on the metallic catalyst surface (mC/cm^2_{geo})
RE	Reference electrode (-)

Symbol	**Description (unit)**
RF	Roughness factor (cm^2_{real}/cm^2_{geo})
RHE	Reference hydrogen electrode (-)
U_M	Catalyst utilisation (%)
ν	Potential scan rate (mV/s)
WE	Working Electrode (-)

THIS PAGE IS LEFT BLANK INTENTIONALLY

4 Test equipment and setup

Generally, the most common experimental configuration for recording cyclic voltammograms is a four measurement electrode configuration, i.e. CE, two RE and (specifically, a reference electrode, R, and a sense electrode, S) and WE connected to a potentiostat.

For a DHE setup, the RE is polarised but it is assumed that the recorded potential is entirely due to WE polarisation. The two RE terminals are typically connected with CE and WE respectively to constitute a two electrode configuration measurement.

THIS PAGE IS LEFT BLANK INTENTIONALLY

5 Test inputs (TIP) and test outputs (TOP)

Test input is a physical quantity which defines the test conditions. There are variable input parameters which are varied during the measurement, and static input parameters which are kept constant during the measurement.

Note, the actual value/range of the inputs depend on the type of LTWE cell and the catalyst configuration as well as whether the anode or the cathode is probed; see Sec. 6 for recommendations.

5.1 Static test inputs

The static inputs for the CV measurement are given in Table 2.

Table 2 Static inputs for the CV measurement

Input	**Symbol**	**Unit**	**Measurement uncertainty**
Start potential	E_{inital}	V	±1%
End potential	E_{final}	V	±1%
Potential scan rate	ν	V/s	±1%
Flow rate per unit of electrode area on CE	Q_{cs}	ml/min//cm$^2_{geo}$	±1% (full scale)
Flow rate per unit of electrode area on WE	Q_{ss}	ml/min//cm$^2_{geo}$	±1% (full scale)
Number of sweep potential voltammetry cycle segments (*)	n_{SEG}	-	-

(*) A minimum of three cycles is recommended with the first cycle commonly disregarded. The second cycle should be taken as CV measurement while the third cycle may serve to validate the measurement.

5.2 Variable test inputs

The variable test inputs are those physical drivers influencing the test object behaviour and are changed in a user-programmable manner during a single experiment with the use of suitable control equipment (potentiostat / galvanostat). The variable inputs for the CV measurement are given in Table 3.

Table 3 Variable input for the CV measurement

Input	**Symbol**	**Unit**	**Measurement uncertainty**
Potential	E	V	±1%

5.3 Test outputs

The primary test output parameters are the measurable physical quantities, which constitute the response of the tested LTWE single cell. The secondary test output parameters are calculated from the primary TOP, see Eqs. (1) to (5). Table 4 provides the details of the output parameter.

Table 4 Test output parameter for the CV measurement

Output	**Symbol**	**Unit**	**Sampling rate**
Current	I	A	≥ 10Hz
Current density	j	A/cm^2_{geo}	≥ 10Hz
Voltammetric charge	Q	mC/cm^2_{geo}	-

Output	**Symbol**	**Unit**	**Sampling rate**
Roughness factor	*RF*	cm^2_{real}/cm^2_{geo}	-
Electrochemically active surface area	*ECSA*	cm^2_{real}	-
Specific ECSA	*sECSA*	cm^2_{real}/g	-
Catalyst utilisation	U_M	%	-

6 Test procedure

6.1 CV measurement for PEMWE

Determination of the ECSA for the oxygen evolution electrode is usually carried out in the driven mode [6]. For a Pt/C and IrO_2 (or IrRu oxide) catalyst, for example, humidified hydrogen and deaerated water is fed to the HER and OER electrode, respectively.

A flow rate of 10 ml/min/cm^2_{geo} and a dew-point temperature equal to cell temperature can be used. In the driven mode, the Pt/C cathode is used as both reference and counter electrode whereas the Ir-Ru oxide anode is the working electrode (and sense electrode), Figure 1.

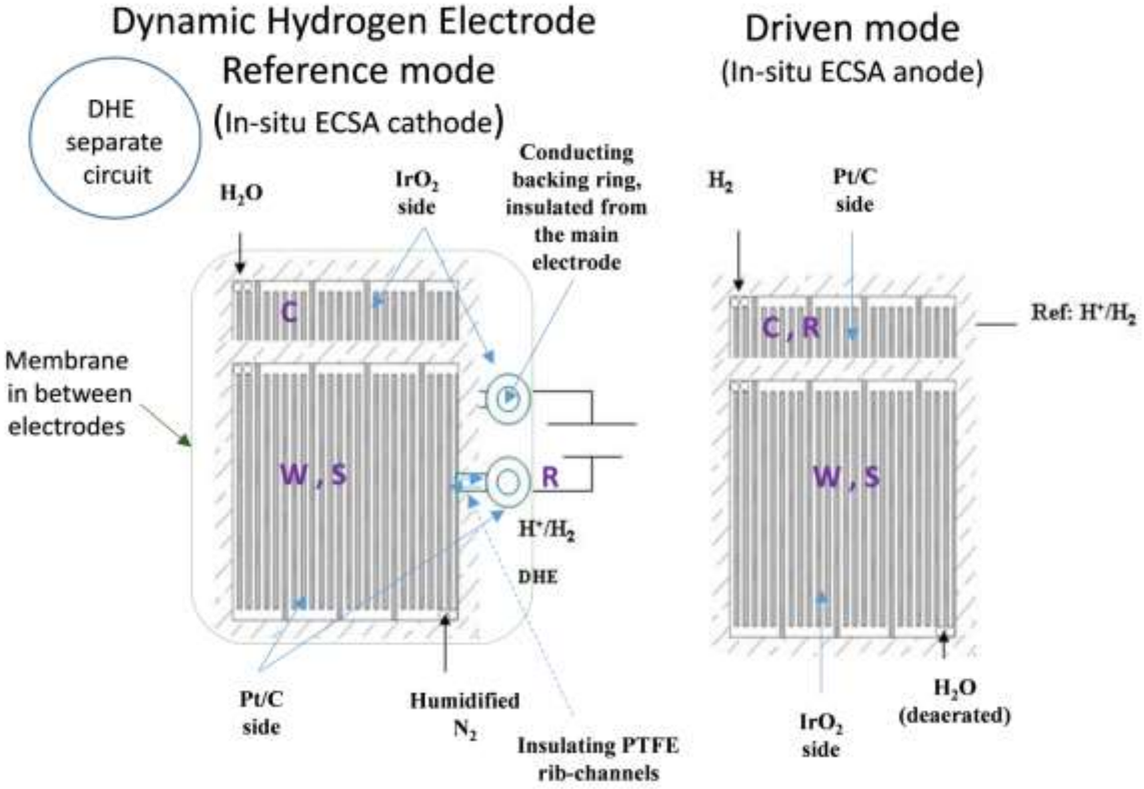

Figure 1 PEMWE configurations for the *in-situ* measurement of the ECSA by CV of the cathode in DHE mode (left) and of the anode in driven mode (right); the arrows (solid blue) indicate the presence of Pt/C and IrO_2 catalyst on their respective electrodes; the capital letters C, R, S and W refer to counter electrode, reference electrode, sense electrode and working electrode, respectively (adapted from [7]).

Since the hydrogen evolution/oxidation is a fast process, being that the current involved in the CV experiment is relatively low, the counter-reference electrode is not significantly polarised and it can be referred to as reversible hydrogen electrode (RHE).

If the ohmic resistance of the cell is sufficiently low, there is no need for IR-drop correction being that the current involved is relatively low.

Recommended conditions are a sweep rate of 20 $mV \cdot s^{-1}$, between 0.4 and 1.4 V vs. RHE, triangular sweep, reference operating temperature and ambient pressure.

Using potentials lower than 0.4 V vs. RHE may produce a significant reduction of the IrO_2 (respectively IrRu oxide) and thus a change of the oxidation state and related adsorption desorption processes.

Generally, the voltammetric charge (sum of anodic and cathodic charge densities) is related to the electrochemical active area or the density of active sites. The coulombic charge varies with the sweep rate; thus, the used scan rate must be reported along with the voltammetric charge value.

Note, the linear variation of the coulombic charge with the square root of the sweep rate allows to qualitatively evaluate the inner and outer surface of the electrode.

For the anode, the active area is obtained from integration of CV profile over the entire potential window similar to Eq. (3), which applies to the hydrogen under-potential deposition (H-upd) charge, with E_1 and E_2 replaced by E_{vert1} to E_{vert2} as lower and upper integration limits.

If the stoichiometry of the adsorption/desorption processes is not known for the IrO_2 (respectively IrRu oxide) anode, the ECSA cannot be determined precisely.

However, the voltammetric surface charge, q* is generally considered an indication of the ECSA even in the case a conversion of the charge into surface area is difficult because the nature of the surface reactions is not known precisely.

In this case, the determined charge may be compared to another measurement carried out under similar conditions.

In situ determination of the ECSA for the Pt/C cathode in PEMWE requires that this electrode (WE) is fed with humidified nitrogen (or inert gas) and alternatively, nitrogen saturated water is present at this electrode [8,9] while the electrode with IrRu oxide (CE) is fed with de-aerated water.

A Dynamic Hydrogen Electrode (DHE) is used as reference electrode, for example, using a configuration similar to that reported in Figure 1.

The DHE (separate circuit) could be based on two small pieces of Pt/C and IrO_2 electrodes contacting the membrane (the same membrane of the main electrodes) on opposite sides. These small electrodes are not in electrical contact with the main electrodes but they are exposed to the same gas or water flows as the main electrodes through PTFE (polytetrafluoroethylene) rib channels (Figure 1).

The two small pieces of Pt/C and IrO_2 electrodes forming the DHE are polarised with a very small current, e.g. a few mA/cm^2 to have a low hydrogen evolution on the negative electrode that acts as reference DHE electrode (Figure 1).

The Pt/C working is preferably polarised in the range 0.02-0.4 V vs. DHE. This is to avoid polarising significantly the counter electrode as well as hydrogen evolution. The lower potential limit can be adjusted (e.g. 0.05 V vs. DHE) to avoid hydrogen evolution; the higher potential limit allows the determination of the double layer current baseline that is subtracted from the integration of the hydrogen adsorption (Pt-H) peaks.

Recommended conditions are a sweep rate of 20 mV/s, a gas flow rate of 10 $ml/min/cm^2_{geo}$, a water flow rate of 1 ml/min/cm, reference operating temperature and ambient pressure.

For determining the ECSA the cathodic sweep profile (adsorption) is integrated after correction for double layer charging, i.e. after subtraction of double layer charging at 0.4 V vs. RHE. For a cathode with a Pt catalyst, a value of 210 $\mu C/cm^2$ [10-12] is taken assuming one monolayer coverage for hydrogen.

For a cathode with a Pd catalyst, the approach is similar; however, the ECSA is preferably determined from the charge involved in the reduction of the oxide layer ($PdO \rightarrow Pd$), from the cyclic voltammograms, assuming a value of 405 $\mu C/cm^2$ for monolayer coverage [13]. In this case, the CV range is from 0.02 (0.05) V to 1.45 V.

In the case of unsupported oxide anode catalysts, the variation of the voltammetric surface charge with the potential scan rate, ν provides information about the existence of less accessible surface regions which become progressively excluded as the sweep rate is increased. For example in the case of Ru-oxide electrodes, q^* usually varies linearly with the $\nu^{-1/2}$. It is thus possible to extrapolate the values of q^* to $\nu = 0$ and $\nu \rightarrow \infty$, respectively.

The extrapolation enables an "inner" surface to be discriminated from an "outer" surface. The former is composed by the regions of poor accessibility for the proton-donating species assisting the surface redox reactions [14].

6.2 CV measurement for AEMWE

Usually, AEMWE consist of non-PGM (platinum group metals) catalysts at both anode and cathode. Commonly, $NiCoO_x$ catalyst is used at the anode and nano-sized Ni-based catalyst is used at the cathode. Adsorption processes are not known precisely for the oxide/hydroxide materials thus the suggested method is the one used for Ir-oxide catalyst in the case of PEMWE. The coulombic charge recorded in the same way for two catalytic systems may then allow for their comparison.

6.3 CV measurement for AWE

Given that AWE catalysts are similar to those used in AEMWE, the same procedure as applied to the latter may also be used for AWE. Surface area measurements are thus similar.

THIS PAGE IS LEFT BLANK INTENTIONALLY

7 Data post processing and representation

For PEMWE cell with Pt/C catalyst at the cathode, the determination of the cathode roughness factor, RF (cm^2_{real}/cm^2_{geo}), ECSA (cm^2_{real}) and specific ECSA (m^2_{real}/g) involves integration of the Coulombic charge under the H-upd peaks associated with the adsorption of hydrogen atoms on the Pt atoms present on the catalyst surface.

The integration of the voltammetric profile in the useful potential window of the voltammogram (between E_1 vs DHE and E_2 vs DHE [8]), corrected for double-layer charging (capacitive component) provides for

$$ECSA = \frac{Q_H}{Q_{HO}} \tag{3}$$

where Q_{HO} is the electric charge per unit area (C/cm^2_{real}) for full coverage of one mono layer of hydrogen on the metallic catalyst surface; e.g. 210 $\mu C/cm^2$ for Pt [10-12] and 311 $\mu C/cm^2$ for Pd [13] and QH is the measured charge in coulombs.

The specific ECSA (sECSA) is the ECSA per unit weight of the catalyst given by

$$sECSA = \frac{Q_H}{Q_{HO} \cdot M} \tag{4}$$

where m is the catalyst mass loading in the electrode (g). The hydrogen desorption charge is given by

$$Q_H = \frac{1}{v} \int_{E_1}^{E_2} IdE. \tag{5}$$

where E_1 and E_2 are the potential integration limits for the potential.

THIS PAGE IS LEFT BLANK INTENTIONALLY

References

[1] N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart, J. L. Dempsey, A Practical Beginner’s Guide to Cyclic Voltammetry, J. Chem. Edu. 95, 2 (2018) 197-206.

[2] S. Brunauer, P.-H. Emmett, E. Teller, Adsorption of gases in multimolecular layers J. Am. Chem. Soc. 60, 2 (1938) 309–319.

[3] A. S. Aricò, P. L. Antonucci, E. Modica, V. Baglio, H. Kim, V. Antonucci, Effect of Pt-Ru alloy composition on high-temperature methanol electro-oxidation, Electrochim. Acta 47 (2002) 3723-3732.

[4] R. Jenkins, R.L. Snyder, Introduction to X-ray Powder Diffractometry, John Wiley & Sons Inc., New York (1996).

[5] G. Tsotridis, A. Pilenga, EU harmonised terminology for low temperature water electrolysis for energy storage applications, EUR 29300 EN, Publications Office of the European Union, Luxembourg, 2018, ISBN 978-92-79-90388-5, doi:10.2760/014448, JRC112082.

[6] S. Siracusano, V. Baglio, N. Van Dijk, L. Merlo, A. S. Aricò, Enhanced performance and durability of low catalyst loading PEM water electrolyser based on a short-side chain perfluorosulfonic ionomer, Appl. Energy 192 (2017) 477-489.

[7] A. S. Aricò, V. Baglio, V. Antonucci, Direct Methanol Fuel Cells, Energy Science, Engineering and Technology, Nova Science Publishers Inc., New York (2010).

[8] E. Brightman, J. Dodwell, N. van Dijk, G. Hinds, In situ characterisation of PEM water electrolysers using a novel reference electrode, Electrochem. Comm. 52 (2015) 1–4.

[9] C. Rozain, E. Mayousse, N. Guilett, P. Millet, Influence of iridium oxide loadings on the performance of PEM water electrolysis cells: Part I–Pure IrO_2 -based anodes, Appl. Catal. B 182 (2016) 153-160.

[10] S. U. B. Ramakrishna, R. D. Srinivasulu, K. S. Shiva, V. Himabindu, Nitrogen doped CNTs supported palladium electrocatalyst for hydrogen evolution reaction in PEM water electrolyser. Int. J. Hydrogen Energy 41 (2016) 20447–20454.

[11] M. K. Naga, R. Balaji, K. S. Dhathathreyan, Palladium nanoparticles as hydrogen evolution reaction (HER) electro catalyst in electrochemical methanol reformer. Int. J. Hydrogen Energy 41 (2016) 46–51.

[12] J. J. Burk, S. K. Buratto, Electrodeposition of Pt Nanoparticle Catalysts from $H_2Pt(OH)_6$ and their Application in PEM Fuel Cells, J. Phys. Chem. C 117 (2013) 18957−18966.

[13] R. Pattabiraman, Electrochemical investigations on carbon supported palladium catalysts, Appl. Catal. A 153 (1997) 9-20.

[14] S. Ardizzone, G. Fregonara, S. Trasatti, Electrochim. Acta 35, 1 (1990) 263-267.

KJ-NA-29285-EN-C

JRC Mission

As the science and knowledge service of the European Commission, the Joint Research Centre's mission is to support EU policies with independent evidence throughout the whole policy cycle.

EU Science Hub
ec.europa.eu/jrc

@EU_ScienceHub

EU Science Hub - Joint Research Centre

Joint Research Centre

EU Science Hub

Publications Office

doi: 10.2760/442574

ISBN 978-92-79-89870-9