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AGREEMENT

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English version

Testing and evaluating the performance of devices for electrocatalytic CO2-reduction

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European foreword

This CEN Workshop Agreement (CWA 18147:2024) has been developed in accordance with the CENCENELEC Guide 29 "CEN/CENELEC Workshop Agreements – A rapid prototyping to standardisation" and with the relevant provisions of CEN/CENELEC Internal Regulations – Part 2. It was approved by a Workshop of representatives of interested parties on 2023-07-20, the constitution of which was supported by CEN following the public call for participation made on 2023-06-16. However, this CEN Workshop Agreement does not necessarily include all relevant stakeholders.

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Introduction

The conversion of CO_2 into chemicals, but also fuels, using energy derived from renewable source has the potential to reduce the use of fossil feedstocks. The production of CO from CO_2 could provide a sustainable CO production method as alternative for the currently dominant fossil-based technologies. The *Reverse Water Gas Shift* (RWGS) reaction is a relatively mature process to perform the CO_2 to CO conversion. This reaction, however, requires the input of hydrogen, which must be produced in a separate process.

Electrochemical conversion of CO_2 to CO is an alternative process which could convert CO_2 to CO in a single conversion process, thereby reducing the number of unit operations.

Two half reactions take part in this process. The reduction of carbon dioxide is usually complemented with the oxidation of water. The effectiveness of a catalytic system depends on the energy efficiency, the selectivity to the desired product, the purity of the product and the system stability.

For both reactions to proceed forward, a significant input of energy is needed, in the form of electrical power, which is converted into energy stored in the chemical bonds of the produced compounds. The total energy required for this electrochemical conversion depends on the energy efficiency of the catalysts and on the electrical and ionic resistances in the system. Indeed, it is the sum of thermodynamic potentials, the overpotentials of both catalysts and the overpotentials related to electrical and ionic resistances. Additionally, the selectivity of the catalyst is influential on the energy demand for this conversion. This catalytic selectivity also affects the percentage of CO_2 that is effectively utilised for the desired product and the amount of undesired side products. Another KPI that is influential for the overall process energy demand is the purity of the produced CO. A high purity CO reduces the required efforts for energy-demanding purification.

Such a process is currently not industrially applied and still in development phase. Many different technologies for electrochemical CO_2 conversion to CO are developed. As there are many applications for CO and many different sources of CO_2, different technologies for CO_2 electroreduction to CO could serve different CO application areas and thus have different desired characteristics.

Today, performance reports of electrolysers in scientific literature are not standardised. This leaves room for multiple interpretations of, for instance, energy efficiency, activity and product purity.

A standard for determining various process characteristics, or KPIs, is thus required. Currently, various KPIs are poorly defined and the determination of KPIs differs throughout various scientific publications. This CWA determines these most influential KPIs for the electrochemical conversion of CO_2 to CO, and enables proper comparison between technologies. Designers and manufacturers of electrocatalytic devices will benefit from these analysis for the different fields of applications.

SUNCOCHEM "*Photoelectrocatalytic device for SUN-driven CO_2 conversion into green CHEMicals*", is a research and innovation project founded by Research Executive Agency of the European Commission under Grant Agreement number 862192. It provides the chemical industry with an alternative to produce oxo-chemicals without using raw materials derived from carbon or oil. The project develops a photoelectrocatalytic tandem reactor to manufacture valuable chemical oxo-products from renewable energies based on CO_2, H_2O and solar energy. SUNCOCHEM project has been the proposer of this CWA and has led its development.

1 Scope

This document specifies procedures and protocols for testing and evaluating the performance of electrolysers for the reduction of CO_2 to CO. This is done by specifying test methods and key parameters for the determination of the performance with regard to:

- production rate per electrode area (see clause 5),

- purity of the produced gas/product gas composition (see clause 6),

- stability of the reactor (see clause 7), and

- energy consumption (see clause 8).

Additionally, protocols for the evaluation of electrolyser performance are specified (see clause 9).

This document does not specify requirements for the construction or the performance of electrolysers for the reduction of CO_2 to CO.It is limited to low-temperature technologies (< 80 °C) and systems with water oxidation as the complementary reaction to CO2 reduction.

This document is intended to be used by organisations and persons manufacturing or using such devices.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at http://www.iso.org/obp/

— IEC Electropedia: available at https://www.electropedia.org/

3.1
anode
electrode at which an anodic reaction predominates

[SOURCE: ISO 8044:2020, 7.1.4]

3.2
anodic reaction
electrode reaction equivalent to a transfer of positive charge from the electronic conductor to the electrolyte

Note 1 to entry: Current enters the electrolyte from the electronic conductor. An anodic reaction is an oxidation process. An example common in corrosion is: $M \rightarrow M^{n+} + ne^-$.

[SOURCE: ISO 8044:2020, 7.1.9]

3.3
catalyst
electrocatalyst
substance that increases the rate of reaction without itself being consumed in the reaction

Note 1 to entry: In the context of electrochemical systems, electrocatalysts play a crucial role in facilitating the conversion of reactants into products by lowering the activation energy required for the reaction to occur. They are essential for improving the efficiency, selectivity, and kinetics of electrochemical processes. Electrochemical reactions, such as the reduction of carbon dioxide (cathode) or the oxidation of water (anode) into oxygen and protons, often have high activation energies. Electrocatalysts accelerate these reactions by providing an alternative reaction pathway with a lower energy barrier.

[SOURCE: ISO/TR 27912:2016, 3.11]

3.4
cathode
electrocathode
electrode at which a cathodic reaction predominates

[SOURCE: ISO 8044:2020, 7.1.3]

3.5
cathodic reaction
transfer of negative charge from the electronic conductor to the electrolyte
Note 1 to entry: Current enters the electronic conductor from the electrolyte. A cathodic reaction is a reduction process, e.g. $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$.

[SOURCE: ISO 8044:2020, 7.1.6]

3.6
CO_2 reduction (CO_2RR)
process of chemically converting CO_2 into other compounds by adding electrons to it

Note 1 to entry: This concept is often associated with environmental and sustainability efforts aimed at mitigating climate change and reducing the impact of greenhouse gas emissions on the planet. In the context of carbon utilisation, CO_2 reduction involves converting carbon dioxide into useful products through processes such as electrochemical reduction or biological methods. This can result in the production of valuable chemicals, fuels, or materials, providing a potential avenue for utilising CO_2 rather than simply mitigating its release.

3.7
electrocatalysis
electrochemically assisted catalysis

[SOURCE: IUPAC Recommendations 2011 [see 10]]

3.8
electrode
electronic conductor in contact with an electrolyte

Note 1 to entry: In the electrochemical sense, the electrode is in fact restricted to narrow regions on both sides of the interface of this system.

[SOURCE: ISO 8044:2020, 7.1.2]

3.9
electrolysis
process in which an electrical potential is applied between two electrodes to drive electrochemical reactions (oxidation and reduction) resulting in electric and ionic current

Note 1 to entry: An example is the oxidation of water to protons and oxygen, and the reduction of these protons to hydrogen (water splitting).

3.10
electrolyte
medium in which an electric current is transported by ions

[SOURCE: ISO 8044:2020, 7.1.1]

3.11
oxidation
process in which a reactant loses one or more electrons

[SOURCE: ISO 8044:2020, 7.1.10]

3.12
reduction
process in which a reactant accepts one or more electrons

[SOURCE: ISO 8044:2020, 7.1.7]

3.13
water oxidation
oxidation of water into oxygen gas and hydrogen ions (protons)

4 Evaluation framework

4.1 CO_2 -> CO reduction process

The electrocatalytic reduction of carbon dioxide (CO_2) to carbon monoxide (CO) is a process that uses electrical energy to convert CO_2 into a valuable and potentially usable chemical product. This electrochemical reaction holds significance in the field of renewable energy and sustainable chemistry. The electrocatalytic reduction of CO_2 involves the use of an electrocatalyst to facilitate the conversion of CO_2 molecules into CO. The reduction half-reaction can be represented as:

$$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-$$
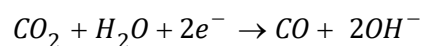
This reaction occurs at the electrode surface in an electrochemical cell.

Electrochemical reduction of CO_2 to CO holds promises for more sustainable production of carbon monoxide than the current dominant fossil-based, providing a means to convert renewable electricity into chemical energy carriers.

Current challenges in this process include low reaction rates, selectivity issues, and the need for stable and cost-effective catalysts. Ongoing research in the field of electrochemistry and sustainable energy aims to address these challenges through advancements in catalyst design, understanding reaction mechanisms, and optimising cell configurations with the goal of developing efficient and economically viable processes for carbon dioxide utilisation and reduction of greenhouse gas emissions.

4.2 Electrolysis setup

The process occurs in an electrochemical cell comprising an electrolyte, a cathode and an anode, often coated with an electrocatalyst. The electrolyte contains ions to facilitate the transport of charge (see Figure 1).

The process can be driven, for example, by solar energy, making it environmentally friendly and reducing dependence on non-renewable energy sources. This latter involves capturing solar energy and converting it into electrical energy using photovoltaic cells. The generated electrical energy is then used to drive the electrocatalytic reduction reaction. In this case, photovoltaic cells are crucial components that convert sunlight into electrical energy. Common materials include silicon-based solar cells and emerging technologies like perovskite solar cells.
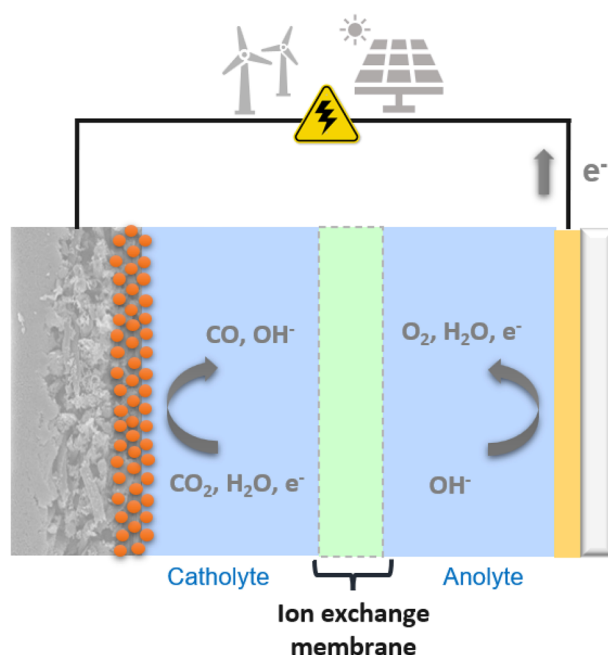
Figure 1 — Electrochemical cell comprised of three compartments (gas and liquid compartments) driven by solar energy

4.3 Electrocatalyst

Electrocatalysts play a crucial role in enhancing the reaction kinetics and selectively promoting the desired CO_2 reduction to CO, minimising side reactions.

Various materials can serve as electrocatalysts, including metals, metal alloys, metal oxides, and organic compounds. Catalyst design is crucial for achieving high efficiency and selectivity.

4.4 Reaction conditions

Reaction conditions, including temperature and pressure, can influence the efficiency of the electrocatalytic reduction. Optimal conditions are determined based on the specific electrocatalyst and system design.

4.5 Equipment

The required equipment is an electrochemical cell configuration, a device that in this case, converts electrical energy chemical energy through redox (reduction-oxidation) reactions. The specific configuration of an electrochemical cell determines how reactants are supplied, how reactions occur, and how electrical energy is generated or consumed.

Key components in an electrochemical cell configuration include:

a) Electrodes:

An electrochemical cell typically consists of two electrodes: an anode and a cathode. The anode is where oxidation (loss of electrons) occurs, while the cathode is where reduction (gain of electrons) takes place.

b) Electrolyte:

The electrolyte is a medium that allows ions to move between the anode and cathode, completing the electrical circuit. It may be a liquid or solid, depending on the type of electrochemical cell.

c) Separator:

A separator is used to physically separate the anode and cathode to maintain the purity of the products in each compartment while allowing ion flow between them. The separator prevents direct contact between the electrodes, reducing the risk of short circuits.

d) Cell casing:

The electrochemical cell is enclosed in a casing or housing, providing structural support and protection for the internal components. The casing is typically designed to be electrically insulating.

e) External circuit:

The external circuit connects the anode and cathode and allows the electrons to flow between them. In the case of non-spontaneous reactions, as it is for electrocatalytic cells, a voltage source is required to make the reactions happen.

f) Voltage source (Electromotive force – EMF):

A voltage source (EMF) is incorporated to drive the non-spontaneous reactions.

g) Flow system:

In continuous-flow systems, reactants are stored in external tanks and are pumped into the cell during the reaction. This flow design allows for scalability and flexible energy storage.

h) Gas diffusion layers:

Gas diffusion layers (GDL) are incorporated to facilitate the diffusion of reactant gases to the electrode surfaces, increasing its concentration.

Understanding and optimising the cell configuration are crucial steps in designing efficient and reliable electrochemical devices for various purposes.

5 Evaluation of the production rate per electrode area

5.1 General

The production rate per electrode area represents the amount of the desired product (e.g., CO) generated per unit area of the electrode over a specified time. It is often expressed in terms of partial current density (current density towards the desired product). The partial current density is obtained by multiplying the current density with the Faraday efficiency (moles of product per moles of electrons).

The following factors influence the production rate:

- Catalyst activity: The choice and activity of the electrocatalyst significantly impacts the production rate.

- Reaction conditions: Factors such as temperature, pressure, and electrolyte composition can influence the electrochemical reaction kinetics and, consequently, the production rate.

The evaluation of the production rate per electrode area in the electrochemical reduction of CO_2 is a critical parameter that provides insights into the efficiency and performance of the electrocatalytic process. This evaluation is essential for understanding how effectively the electrocatalyst converts CO_2 into desired products, such as CO or other value-added chemicals. Higher production rates indicate improved efficiency and performance, contributing to the economic viability and practical application of the technology. The production rate per electrode area can be used as a benchmark to compare the performance of different catalysts, electrode materials, and experimental conditions.

5.2 Calculation of Production Rate

a) **Current Density (j):** The current density is a key parameter and is calculated by dividing the applied current (I) by the electrode area (A).

$$j = \frac{I}{A}$$

where,

I is the current in A;

A is the electrode area in cm²

b) **Faraday Efficiency (FE):** Faraday efficiency represents the fraction of electrons used in the desired CO_2 reduction reaction. It is calculated by dividing the actual moles of product formed by the theoretical moles of product calculated from the total charge passed.

$$FE = \frac{Actual\ moles\ of\ product}{Theoretical\ moles\ of\ product} = \frac{z * n * F * 100}{Q}$$

where:

z is the number of transferred electrons ($z = 2$ for electroreduction of CO_2 to CO);

F is Faraday's constant (96.485 C/mol);

n is the number of moles of the product (mol);

Q is the total charge (C).

c) **Partial current density (j_{CO}):** This is determined by multiplying the current density by the Faraday efficiency.

$$j_{CO} = j * FE$$

d) **Production Rate:** is determined by the following equation:

$$PR = \frac{I}{z * F} * FE$$

where,

PR [mol/s]

5.3 Normalised Production Rate

To compare different electrochemical systems or conditions, the production rate is often normalised per unit electrode area.

- For electrode area (e.g., cm^2):

$$PR_{normalised,area} = \frac{PR}{A}$$

6 Evaluation of the purity of the produced gas/produced gas composition and quantity

6.1 General

The electrocatalytic performance of the electrodes is evaluated under different potential and current conditions. The purity of produced compounds and their composition are crucial factors in assessing the selectivity and efficiency of the electrocatalytic process. Therefore, an appropriate automated gas collection system is required to capture and analyse the evolved gases during the electrocatalytic process to ensure that the collected gas represents the system's performance.

- Gas chromatography (GC) is a widely used technique for separating and analysing gas mixture components. The evolved gas from the electrochemical cell is continuously sent into the chromatograph. It takes a sample, and as it moves through a column, different components separate based on their chemical properties. Detectors at the end of the column identify and quantify each separated component.

- Mass spectrometry (MS) identifies and quantifies compounds based on their mass-to-charge ratio. It is coupled with gas chromatography to enhance the identification capabilities. GC-MS has a wide variety of applications because of its ability to detect various types of molecules with high accuracy. The liquid samples are taken directly from the electrochemical cell during the CO2 electro-reduction test. Specifically, some millilitres are taken before and after applying potential or current. Subsequently, they are analysed without undergoing any treatment. The type of analysis performed to quantify the products is the SIR (Selected Ion Recording). In this way, the spectrum is integrated into the desired masses, amplifying the signal of the masses of the analyte of interest and reducing the rest to zero.

When testing the purity of gases or analysing gas compositions, it is essential to consider factors such as detection limits, accuracy and precision. Choosing the appropriate method depends on the nature of the gases involved and the precision required for the analysis. Instrumentation shall be regularly calibrated to ensure accurate and reliable measurements. Analysis shall be done in accordance with subclause 6.2 and following the instructions of the equipment manufacturer to measure gas.

The outgoing gas flow rate can be measured accurately in two ways: i) by installing a flow meter in a small pipe parallel to the cell outlet tube or ii) by mixing the outgoing gas stream from the electrolyser with a constant flow of N_2 as an internal standard. This mixture of gases should be introduced into a gas chromatograph. Determination of the absolute volumetric flow after electrolysis should be conducted based on changes in the concentration of N_2 standard as detected by the TCD.

6.2 Considerations for gas sampling

- Leaks and atmospheric diffusion in the sampling system result in a loss of produced gas and influence the composition of the sample (the direction of diffusion is determined by the difference of partial pressure of the component). Therefore, all the connections and joints shall be checked before the first use. The evacuation of residual O_2 and N_2 in the system through purging should be done to avoid contamination. The complete evacuation can be verified by monitoring the concentration.

- Gas inhomogeneity will affect the concentrations, causing errors. Turbulence in the system is suggested for quick gas mixing.

- The outgas products from the cell can contain condensable gases. Their condensation could affect the collection of representative samples. Then, to prevent that factor, heating the sampling line is suggested, and the pressure drop across the sampling line should be minimised.

For further information about gas sampling see ISO 19230:2020.

7   Evaluation of the stability of the reactor

7.1 General

To date, the performances of a CO_2 electrolyser have been evaluated based on three main figures of merit, namely Faradaic Efficiency (selectivity), current density (activity) and overpotentials (energy efficiency). The majority of the electrochemical reactors have been tested for hundreds of hours or less, but durability is perhaps the most important metric to move the technology to a higher readiness level (see [1]). A recent study highlighted that CO_2RR systems need to operate beyond 20.000 h (see [2]). In fact, the importance of a stable system lies in reducing maintenance and replacement costs.

This chapter provides an overview of the degradation mechanisms and offers a guidance to their determination and to mitigation/recovery strategies which can be put in place.

Stability of the electrolyser can be limited by several factors: assembly error, degradation of the electrolyser components and spontaneous events (see [3]).

- Assembly error is related to an initial failure of the cell due to mounting stages: the effects of an under or over compression span from an increase in the cell resistance (due to the larger distance between the components) to microcracks of the components and blocking of CO_2 diffusion.

- The degradation of cell components is related to the instability during operations and accumulations within the components. During operations, electrode flooding may occur when electrolyte or liquid products block the pores of the electrode and prevent CO_2 diffusion. Likewise, passivation phenomena or catalyst loss may be observed at the anode side. Moreover, the use of salt-based electrolyte implies that during operations the solubility limit may be reached, eventually causing salt precipitation within the pores of the electrode.

- Spontaneous events are immediate failures (e.g., breakage of the electrodes, holes in the ion exchange membrane) that may occur as consequence of pressure increase and gas products build-up.

7.2 Determination of degradation mechanisms

The economic viability of electrochemical systems requires them to work thousands of hours exhibiting a decay of key performance parameters below 10% (see [1]). From durability testing it is possible to obtain information of paramount importance, through which a pathway toward the development of more lasting electrolysers can be set out.

a) Pre-testing

It can consist of a set of analytical techniques with the aim of fully characterising the fabricated electrode in terms of morphology (electron microscopy, tomography) and composition (x-ray spectroscopy, x-ray diffraction). Additionally, electrochemical surface area and cell resistance can be determined, and its eventual variations may be indicative of degradation mechanisms. A reference is created for post-testing operations.

b) Long-term testing

Developing a stable and durable electrolyser requires monitoring the system continuously for thousands of hours (equivalent to months of operation), which is not practical. Accordingly, the characterisation of cell performance might be carried out by means of accelerated durability and/or stress tests (respectively ADT and AST), taking as reference the protocols developed and validated by the U.S. Department of Energy (DOE) for proton exchange membrane fuel cells (PEMFCs, see [4]). In addition to pre- and post-testing analyses, the regular monitoring of Faraday efficiencies and cell potential is insightful.

c) Post-testing

The characterisation techniques selected in the pre-testing stage should be repeated after the long-term test. What matters at this stage is the sequence of the post-testing techniques since some of these may cause a change in the morphology/composition and alter the results. The more analyses are carried out, the more detailed will be the picture of degradation mechanisms that the system experimented.

Among the performance indicators (see [11]), one of the most suited for assessing the *degradation rate* in low-temperature water electrolysers is cell voltage at reference operating conditions (T, p, I). The increase in the cell voltage is expected over time and is experimentally monitored. It can be broken down into reversible and irreversible voltage increases. However, this parameter evaluates only partially the degradation rate through the cell. Thus, it is usually complemented by the stability factor SF_j at a given current density j, defined as the inverse product of the cell voltage increase rate and the initial cell voltage deviation.

7.3 Mitigation/Recovery Strategies of cell components

The degradation mechanisms can be broken down into physical and chemical changes. The formers are generally irreversible, while the latters may be reversed. Several and common degradation mechanisms have been discussed in the literature and, for any of those, attempts to reverse them have been proposed. The table below summarises the observed mechanisms and demonstrated mitigation/recovery strategies.

Table 1 — Summary of degradation mechanisms seen in literature and demonstrated mitigation/recovery strategies, if any (adapted from [1])

Degradation mechanism	Negative effects on cell performance	Demonstrated mitigation/recovery strategies
Physical degradation mechanisms		
Catalyst particle agglomeration.	Increase of cell resistance. Permanent loss of activity.	-
Catalyst leaching.	Loss of CO_2RR activity.	-
GDL erosion.	Hydrophobicity loss.	-
Blocking of electrode pores.	Loss of CO_2RR activity.	-
Chemical degradation mechanisms		
Catalyst poisoning.	Decrease in FE.	Applied (+) current or potential. Electrolyte purification.
Binder degradation.	Flooding. Loss of CO_2RR activity.	Wetproofing optimisation.
GDL carbon corrosion.	Increased charge-transfer resistance. Loss of catalyst.	-
Carbonate formation.	Flooding. Loss of CO_2RR activity.	Periodically rinsing electrode.

7.4 Monitoring the state-of-health of the electrolyser

In-operando tools are needed to assess uniquely the performance of cell components/electrochemical interfaces at industrial conditions. A multi-electrode technique has been proposed to break down overpotentials and control or mitigate convolution errors, thus providing better accessibility to each interface and enriching stability testing methods (see [5]).

In-line multi-sine electrochemical impedance spectroscopy (EIS) can be used as powerful tool during long-term operations to provide additional electrochemical parameters and detailed information on the changes over time, allowing the early recognition of failure modes and their prompt correction. This technique applies an alternating current (AC) modulation to the electrochemical systems operating at a direct current (DC) steady state. The quantity and quality of information that can be derived depends on the complexity of the equivalent electrical circuit used to fit the EIS data. The development of a framework for the isolation and monitoring of specific electrochemical interfaces offers the possibility to prevent irreversible degradation mechanisms, to isolate a single cell in a stack, and valuable insights for the further optimisation of the cell components. Once developed, this monitoring technique can be adapted to larger cells and stacks, accompanying their technological maturation.

8 Evaluation of the energy consumption

8.1 General

The evaluation of the performance of co-electrolysers for CO_2 to CO conversion involves considering factors like Faraday efficiency (FE), overpotential, and economic feasibility (energy efficiency & electrical power consumption). Energy efficiency (EE) is a measure of how effectively energy is used, while electric power consumption (EPC) quantifies the amount of electrical energy used. Improving energy efficiency can help reduce electric power consumption and contribute to sustainability efforts. It's essential to consider both aspects for effective energy management and conservation. Ongoing research aims to improve the efficiency and cost-effectiveness of this process for a sustainable and viable carbon reduction strategy.

Due to the high cost of electrolysis units, the cells or stacks must produce as much CO gas during their lifetime as possible. Thus, some level of voltage degradation (resistance increase) is acceptable, as long as the electrolysis unit is producing gas satisfying some pre-determined system output requirements (i.e. gas purity and production rate). Similarly, some loss of FE may be acceptable, if the downstream separation system is able to handle the increasing amounts of H_2 or other undesired side-products originating from the electrolysis unit.

8.2 Faraday Efficiency

As indicated above (see 5.2), Faradaic efficiency is a key metric that measures the ratio of electrons used for the desired CO_2 reduction reaction (i.e. CO) to the total electrons supplied. A high Faraday efficiency indicates a more selective and efficient conversion.

8.3 Overpotential

Overpotential is the additional potential applied beyond the thermodynamic requirement for the electrochemical reaction. Minimising overpotential is essential to reduce energy losses in the process.

8.4 Area-specific resistance (ASR)

It is the slope of the polarisation curve (j vs. V) at a given current density. ASR is commonly used to characterise the performance of solid oxide electrolysers (SOEC) but is rarely used for low-temperature cells. For direct comparison, the ASR was estimated at $j_{CO} = 200 \pm 30$ mA cm^{-2} for each of the electrolysers.

8.5 Energy Efficiency (EE)

8.5.1 Electrical Energy Efficiency (EE)

Energy efficiency refers to the ratio of useful energy output to the total energy input in a system. It measures how effectively a system or device converts input energy into useful output energy. It is a commonly used performance metric for low T electrolysers because EE does not consider the heating energy demand.

Improving energy efficiency is crucial for reducing energy consumption, lowering costs, and minimising environmental impact. It is often expressed as a percentage, with higher percentages indicating better efficiency.

The general formula for calculating electrical energy efficiency is typically given by:

$$EE = \frac{Useful\ Energy\ Output}{Electrical\ Energy\ Input} \times 100$$

In terms of co-electrolysers, the efficiency of converting applied electric potential into the desired product (CO), combining the effect of losses due to non-ideal selectivity (FE) and polarisation losses (η), is given by:

$$EE = \frac{E^O * (FE)}{E^O + \eta} = \frac{E^O * (FE)}{E}$$

where:

E^o is the reversible cell voltage (V);

FE is Faradaic efficiency;

η is the cell overpotential (V);

$E = E^o + \eta$ is the cell potential at the desired current density (V).

In the case of a photoelectrochemical reactor, the energy efficiency of the device is:

$$EE = \frac{E^O * (FE)}{E} * \frac{j_{sc} * E_{rxn} * FE}{P_{in}} = \eta_{EC} * \eta_{PEC}$$

where:

j_{sc} is the photocurrent density at short circuit (mA cm^{-2});

FE Faradaic efficiency of the solar-generated product;

E_{rxn} is the voltage required to drive the reaction (V);

P_{in} is the incident solar power (mW cm^{-2}).

8.5.2 Total Energy Efficiency (TEE)

In the chemical industry, the total energy (TEE) is typically defined as the ratio of the lower heating value (LHV, also called the net calorific value) of the desired product to the energy needed for its synthesis and purification ($E_{synthesis}$ and $E_{purification}$, respectively), as shown below:

$$TEE = \frac{LHV_{product}}{E_{synthesis} + E_{purification}}$$

For electrolysers, the energy needed to synthesise a target product is defined as the enthalpy change (ΔH) divided by the Faraday efficiency for the desired product ($FE_{product}$), as represented here:

$$E_{synthesis} = \frac{\Delta H}{FE_{product}}$$

The enthalpy change is the sum of the Gibbs free energy change (ΔG) and the entropic contribution, which is the product of temperature (T) and entropy change (ΔS), as shown in the follow equation:

$$\Delta H = \Delta G + T * \Delta S$$

The Gibbs free energy required for a target product is defined as the negative product of the cell potential (E_{cell}), the Faraday constant (F), and the number of electrons transferred in the reaction to produce the target product ($n_{product}$), as represented by:

$$\Delta G = - E_{cell} * F * n_{product}$$

Combining equations above results in the following equation:

$$TEE = \frac{LHV_{product}}{\dfrac{-E_{cell} * F * n_{product} + T * \Delta S}{FE_{product}} + E_{purification}}$$

The energy efficiency is mainly affected by the energy required for electrochemical synthesis. At low temperatures (below 100°C), the entropic contribution is generally minimal. Thus, energy efficiency is largely dictated by the cell potential and the Faraday efficiency for the desired product. Faraday efficiencies greater than 50% are frequently observed. In such cases, the energy efficiency of the synthesis process is primarily determined by the cell potential of the electrolyser.

The measured cell potential (E_{cell}) is typically composed of the contributions of half-cell potentials ($E_{cathode}$ and E_{anode}) and the potential of the membrane ($E_{membrane}$), as represented here:

$$E_{cell} = E_{cathode} + E_{anode} + E_{membrane}$$

The electrode potentials ($E_{electrode}$), whether for the cathode or anode, consist of several components: the half-reaction potential ($E_{half\text{-}reaction}$), which is adjusted for the local pH; the overpotential due to electron transfer and reaction kinetics on the catalyst ($\eta_{ct+reaction}$); and the Galvani potential difference ($\Delta\Phi$) from ion transfer between the electrode and the electrolyte/membrane.

$$E_{cathode} = E_{half\text{-}reaction,cathode} + \eta_{ct+reaction,cathode} + \eta_{CO2\ mass\ transfer} + \eta_{products\ mass\ transfer} + \Delta\Phi_{cathode}$$

$$E_{anode} = E_{half\text{-}reaction,anode} + \eta_{ct+reaction,anode} + \eta_{CO2\ gas\ bubblesr} + \Delta\Phi_{anode}$$

$$E_{membrane} = E_{pH\ dependant} + \Delta\Phi_{membrane} + E_{thermodynamic,\ water\ dissociation\ (only\ Bipolar\ membranes\ (BPM))} + \eta_{water\ dissociation\ (only\ BPM)}$$

8.6 Electric Power Consumption (EPC)

Electric Power Consumption refers to the amount of electrical energy consumed by a device, system, or process over a specific period. It is usually measured in units such as kilowatt-hours (kWh) for household or industrial electricity consumption.

Monitoring electric power consumption is crucial for understanding and managing energy use. It helps in optimising energy efficiency, identifying areas for improvement, and controlling costs.

The formula for calculating electric power consumption is given by:

$$EPC = Power\ (in\ kW) * Time\ (in\ hours)$$

To show the result in kilowatt-hours, this can be further expressed as:

$$EPC = \frac{Power\ (in\ kW) * Time\ (in\ hours)}{1000}$$

The amount of electric energy [kWh] required for producing 1 Nm^3 of product gas, i.e. CO, is given by:

$$EPC = \frac{E * n * F}{FE * V_m}$$

where:

    E is the cell voltage;

    n is the number of transferred electrons (n = 2 for electroreduction of CO_2 to CO);

    F is Faraday's constant;

    FE is Faraday efficiency;

    V_m is the molar volume of ideal gas under normal conditions.

9 Protocols for the evaluation of electrolyser performance

9.1 General

This chapter offers protocols for the evaluation of electrolyser performance and the assessment of its robustness and durability.

The type of test which have been developed by the U.S. Department of Energy (DOE) for proton exchange membrane fuel cells (PEMFCs) depends on whether the objective is to test the system in startup/shutdown mode or in run mode (driving) (see [4]). The two conditions correspond to triangle or step cycles (cyclic voltammetry) and to constant current/potential (chronopotentiometry or chronoamperometry), respectively. The DOE's protocols can be therefore adapted to electrochemical CO_2 reduction reactions, with galvanostatic/potentiostatic measurements that would be used for continuous production, while cyclic voltammetry would mimic real fluctuations in the renewable energy loads.

Key performance parameters need to be monitored before/after (e.g., electrochemical active surface area, polarisation curves, composition and morphology of the catalyst) and throughout (Faradaic Efficiency, cell components overpotentials) the electrochemical operations.

Before embarking on accelerated tests, stable cell operation for 50 h with a drop in performance less than 10% should be targeted (see [4]).

The *EU harmonised protocols for testing of low-temperature water electrolysers* (see [11]) established a methodology for assessing the impact of deviations in the input parameters –from reference operating conditions– on the cell performance and durability. Six types of stressors, that is the factors causing deviations, were identified: stressors due to operating conditions, stressors due to load cycling, stressors due to mechanical effects, stressors due to seal leakage, stressors due to water quality and stressors due to environmental conditions.

By relating changes in the output parameters after accelerated protocols to changes after standard testing (that is usual long-term test) it is possible to estimate the real lifetime of the electrolyser.

9.2 Protocol for electrolyser performance under variable loads

1. *Physico-chemical characterisation of the electrodes*. This allows to create a reference of the catalyst morphology and composition.

2. *Activation and conditioning of cell components according to cell/components manufacturers.*

3. *Polarisation curve under nitrogen flow*. This allows to create a reference for the electrochemical behaviour of the electrode in inert environment, also referred to as "curve at the Beginning of Test (BoT)" (see [11]).

4. *Polarisation curve under carbon dioxide flow.* This allows to create a reference for the electrochemical behaviour of the electrode in reactive environment, also referred to as "curve at the Beginning of Test (BoT)" (see [11]).

5. *Constant current/potential measurements at target conditions and in-line electrochemical impedance spectroscopy.* This allows to create a reference for the (i) Faradaic efficiency of gas and liquid products, (ii) the outlet streams composition and rates, (iii) energy consumption of the electrolyser, (iv) cell components resistances and charge transfer.

6. *Cycling stress test[1].* Extreme values might be potential/current corresponding to lower energy load and potential/current corresponding to the target current density.

7. *Polarisation curve under carbon dioxide flow.* Useful data for monitoring the changes in the metrics, also referred to as "curve at the End of Test (EoT)" (see [11]).

8. *Constant current/potential measurements at target conditions and in-line electrochemical impedance spectroscopy.* Useful data for monitoring the changes in (i) Faradaic efficiency of gas and liquid products, (ii) the outlet stream composition and rates, (iii) energy consumption of the electrolyser, (iv) cell components resistances and charge transfer.

9. *Physico-chemical characterisation of the electrodes.* Useful data for monitoring the changes in the catalyst morphology and composition.

9.3 Protocol for electrolyser performance under constant loads

1. *Physico-chemical characterisation of the electrodes.* This allows to create a reference of the catalyst morphology and composition.

2. *Activation and conditioning of cell components according to cell/components manufacturers.*

3. *Polarisation curve under nitrogen flow.* This allows to create a reference for the electrochemical behaviour of the electrode in inert environment, also referred to as "curve at the Beginning of Test (BoT)" (see [11]).

4. *Polarisation curve under carbon dioxide flow.* This allows to create a reference for the electrochemical behaviour of the electrode in reactive environment, also referred to as "curve at the Beginning of Test (BoT)" (see [11]).

5. *Constant current/potential measurements at target conditions and in-line electrochemical impedance spectroscopy.* This allows to create a reference for the (i) Faradaic efficiency of gas and liquid products, (ii) the outlet stream composition, (iii) energy consumption of the electrolyser, (iv) cell components resistances and charge transfer.

6. *Extreme conditions test[1].* Extreme conditions can be either higher salt concentrations in the electrolyte or higher current/potential values in shorter timescale to keep constant the total charge.

7. *Polarisation curve under carbon dioxide flow.* Useful data for monitoring the changes in the metrics, also referred to as "curve at the End of Test (BoT)" (see [11]).

8. *Constant current/potential measurements at target conditions and in-line electrochemical impedance spectroscopy.* Useful data for monitoring the changes in (i) Faradaic efficiency of gas and liquid products, (ii) the outlet stream composition and rates, (iii) energy consumption of the electrolyser, (iv) cell components resistances and charge transfer.

9. *Physico-chemical characterisation of the electrodes.* Useful data for monitoring the changes in the catalyst morphology and composition.

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