

# Constant Tafel Slope Voltage Breakdown Analysis Method

The realm of sustainable energy is evolving at a rapid pace and at the forefront of this evolution is hydrogen. Known for its environmental friendliness and sustainability, hydrogen serves as a potent energy carrier with the potential to revolutionize energy systems, transport, and a significant portion of the chemical industry. This transformation can be achieved without any CO<sub>2</sub> emissions, provided hydrogen production is driven by renewable energies utilizing Proton Exchange Membrane (PEM) water electrolysis (PEMWE).

In the past, the production of hydrogen saw the extensive use of Ir-based catalysts in the anode catalyst layer (CL). These catalysts were favored for the oxygen evolution reaction (OER) due to their high activity and stability under relatively harsh anodic conditions. However, the goal to reduce hydrogen production costs has necessitated the reduction of catalyst usage in the anode CL. This presents a challenge: how to decrease the anode catalyst loading while simultaneously maintaining or even enhancing performance and durability.

It has been recognized that the anodic interface between the CL and the porous transport layer (PTL) has a significant influence on both the performance and durability of PEMWE cells. For instance, a reduction in catalyst loading usually results in a decrease in CL thickness and a relatively poor electrical in-plane conductivity.

Addressing these challenges requires an in-depth understanding of the relationship between structure properties and performance. Traditionally, to investigate this interface, a voltage breakdown analysis (VBA) method has been employed to differentiate between different sources of overpotential. However, this approach has been found to be less effective particularly when using low Ir loadings. The VBA method often results in inconclusive OER kinetic parameters such as the apparent exchange current density and the determined three main overpotentials (kinetic overpotential, mass transport overpotential, and ohmic overpotential).

To overcome these weaknesses of the prior art, a new method needs to be proposed. The kinetic parameter, or the specific electrochemical active surface area (ECSA), measures the number of active Ir(oxide) sites. Techniques for experimental ECSA determination of platinum electrodes have been established using cyclic voltammogram (CV) measurements, such as those used for fuel cells. Regrettably, these measurement methods cannot be directly applied to Ir(Ox) electrodes utilized in PEMWE.

Traditionally, a VBA method is used for differentiation between the main overpotentials (ohmic, kinetic and mass transport losses) and the access kinetic parameters. By using the mentioned method for the PEMWE cells (that have the same cell set up and anodic catalyst type and batch, but different anode catalyst loadings), the Tafel slope,  $b_1$ , increase with the decreasing of Iridium loading, Figure 1.

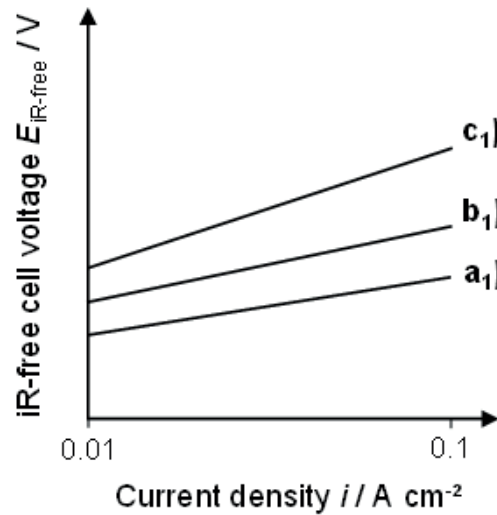


Figure 1. Tafel plot of different anodic catalyst loadings a1) highest loading b1) medium loading c1) lowest loading for VBA method.

Through the method of extrapolating the fitted Tafel line to equilibrium conditions, it is feasible to ascertain the apparent exchange current density  $i_0$ . However, from a fundamental perspective, this process yields an inaccurate trend for the apparent exchange current density, as evidenced by the sequence  $i_0(a_1) < i_0(b_1) < i_0(c_1)$ , as seen in Figure 2 below.

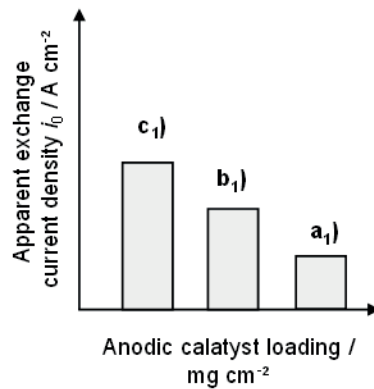


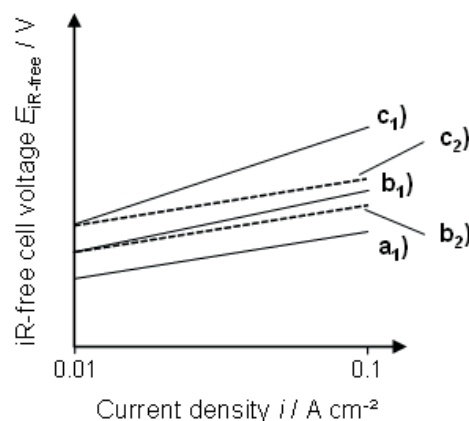
Figure 2. Determined apparent exchange current density values as a function of anodic catalyst loadings a1) highest loading b1) medium loading c1) lowest loading for VBA method.

This proposal aims to develop an adapted analysis method: Constant Tafel slope voltage breakdown analysis (CT-VBA) method. The main objective is to create a more precise study on kinetic parameters such as: apparent exchange current density, as well as the relations between structure catalyst loading and performance.

The method can be easily explained by dividing it into steps:

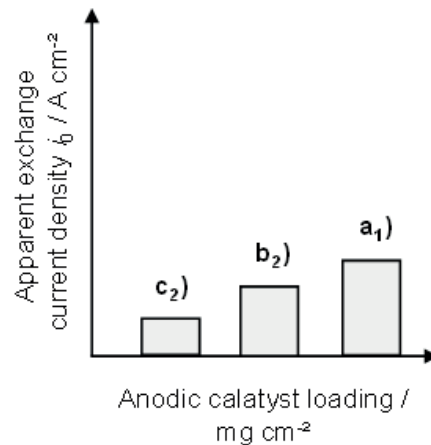
- 1) Initially, the most successful experiment, characterized by the highest anodic catalyst loading and the most efficient PTL, is designated as the reference case. In this context, it is presumed that the losses associated with mass transport are insignificant within the low current density area utilized to fit the Tafel lines.
- 2) The Tafel slope  $b_r$  of the reference case is used for all other experiments and transferred to all other experiments at a fixed setpoint e.g.  $0.01 \text{ A/cm}^2$ .
- 3) The Tafel slope of the reference case is then used for extrapolating the Tafel line from  $iR$ -free cell voltage value at fixed setpoint e.g.  $0.01 \text{ A/cm}^2$  for each case.
- 4) Consequently, by definition, only parallel shifts can be observed using the proposed CT-VBA method.

The implementation of the CT-VBA method yields modified Tafel lines  $b_2$  and  $c_2$  in place of  $b_1$  and  $c_1$ . These adjusted Tafel lines possess the same Tafel slope as the reference case, albeit they are parallelly shifted towards a higher potential, Figure 3.



*Figure 3. Tafel plot of different anodic catalyst loadings a1) highest loading b1) medium loading c1) lowest loading for VBA method and b2) medium loading c2) lowest loading for CT-VBA method.*

By using the CT-VBA method, the apparent exchange current density values (found in Figure 4) and the kinetic and mass transport overpotential can be calculated.



*Figure 4. Determined apparent exchange current density values as a function of anodic catalyst loadings a1) highest loading b2) medium loading c2) lowest loading for CT-VBA method.*

The application of the CT-VBA method enables a more accurate determination of kinetic parameters ( $b$ ,  $i_0$ , etc.). Notably, the CT-VBA method's utility isn't limited to accessing kinetic parameters within a single cell setup (where the only variable is the anode catalyst loading), but it can also be employed with diverse cell components, such as anodic PTLs, provided that the same catalyst type and batch are used.

In such scenarios, the reference case is identified as the optimal performing combination, which includes the highest anode catalyst loading and the most efficient PTL type.

In summary, the invention possesses several noteworthy characteristics. Firstly, it enables the transfer of the Tafel slope from a reference case, which includes the highest anode catalyst loading and the best performing PTL type, to experiments with a lesser anode catalyst loading at a fixed setpoint.

Secondly, it facilitates the computation of the apparent exchange current density with these Tafel lines. Thirdly, it allows for the calculation of the kinetic and mass transport overpotential using these Tafel lines.

Lastly, the invention employs the CT-VBA method for the screening of anode catalysts with varying anode catalyst loading and different PTL types. These attributes collectively contribute to the invention's innovation and potential for significant impact in its relevant field.