

IN SITU PEM FUEL CELL ELECTROCHEMICAL SURFACE AREA AND CATALYST UTILIZATION MEASUREMENT

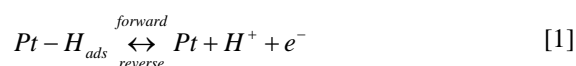
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The article introduces the use of cyclic voltammetry (CV) for evaluation of catalyst utilization and electrochemical surface area of fuel cell electrocatalysts.

A typical proton exchange membrane fuel cell (PEMFC) catalyst layer is a porous, three dimensional structure consisting of carbon support, platinum (Pt) or Pt-alloy catalyst and ionomer such as Nafion[®], all in intimate contact. The carbon support enhances the bulk electronic conductivity of the electrode and dispersion of the catalyst nanoparticles. The ionomer serves to bind the electrode layer and facilitate proton conduction to the reaction site. Voids allow for mass transport of gas or liquid phase reactants and products to and from the carbon-supported electrocatalyst. The electrochemical activity (current/nominal area) of the catalyst layer is a function of the extent and quality of the three phase boundaries where reactants, ionically and electrically conducting material and active catalyst sites are in intimate contact. Electrochemical surface area and catalyst utilization are critical performance metrics for catalyst and membrane electrode assembly (MEA) developers and manufacturers.

The technique for determining the *electrochemical surface area* (ECSA) of fuel cell electrodes by CV analysis has been used for several decades. The procedure involves cycling the electrode of interest over a voltage range where charge transfer reactions are adsorption-limited at the activation sites. That is, the electrode potential is such that the number of reactive surface sites can be obtained by recording the total charge required for monolayer adsorption/desorption.

Common reactions used when characterizing PEMFC electrodes are the hydrogen adsorption/desorption (HAD)¹,



or the oxidative stripping of adsorbed carbon monoxide²,

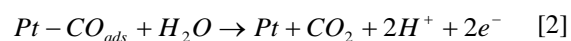


Figure 1 shows a typical CV voltammogram of the HAD reaction. The process of interest is the electroreduction of protons and adsorption of hydrogen on the catalyst surface, that is, reaction [1] in the reverse direction. The hydrogen adsorption charge density (q_{Pt} in Coulombs/cm²) due to this reaction determined from the CV experiment is used to calculate the ECSA of the fuel cell electrode.

The electrochemical surface area (ECSA) of the Pt catalyst is calculated from the charge density q_{Pt} (C/cm²_{electrode}) obtained from the CV experiment; the charge required to reduce a monolayer of protons on Pt, $F = 210 \mu\text{C}/\text{cm}^2_{Pt}$ ^{1,3}; and the Pt content or loading in the electrode, L in g_{Pt}/cm²_{electrode}.

$$ECSA (\text{cm}^2_{Pt} / \text{g}_{Pt}) = \frac{q_{Pt}}{F \cdot L} \quad (1)$$

Not all of the catalyst used to make the fuel cell electrode is accessible to reactants (e.g., protons and oxygen at the cathode) and/or is in electrically contact and thus is not able to participate in the electrochemical reaction. The fraction of the catalyst that is available to participate in electrode reactions is given by the ratio of ECSA to the specific area of the catalyst obtained by the catalyst manufacturer using chemisorption or other *ex situ* techniques (also in cm²_{Pt} / g_{Pt}). This ratio is referred to as *utilization*. Higher catalyst utilization is better.

Utilization is an idealized condition because the very low reaction rate used during the ECSA measurement results in negligible transport limitations. In a fuel cell operating at a practical current density, oxygen and/or proton transport resistances could decrease the amount of catalyst that participates in the cathode reaction⁴, effectively decreasing utilization.

Fuel cell electrodes may be examined for their electrocatalytic performance by *ex situ* or *in situ* voltammetry experiments. In the case of *ex situ* experiments, also known as half-cell experiments, the properties of the electrode are evaluated using a standard three-electrode cell where an aqueous solution (e.g., perchloric acid) simulates the proton-conducting electrolyte in a PEMFC. Half-cell experiments are a convenient and relatively fast method of screening electrocatalysts but are not suitable for evaluation of fuel cell electrodes under operating conditions.

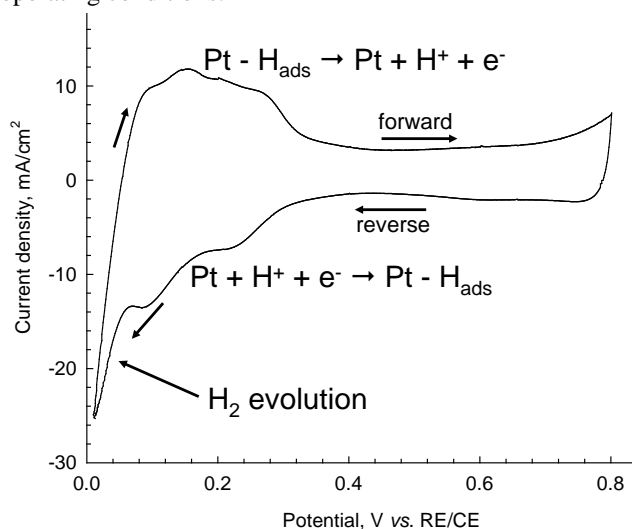


Figure 1. Cyclic voltammogram of PEM fuel cell catalyst layer for ECSA analysis by hydrogen adsorption/desorption. Conditions: Scan rate = 40 mV/s; Cell: 35 °C; 100% RH anode/cathode; 1 atm.

In Situ ECSA and Catalyst Utilization Measurement

In situ experiments use a two-electrode configuration in which one of the electrodes of the fuel cell serves as both a counter electrode and a pseudo-reference electrode. Typically, the electrochemical activity of the fuel cell cathode is of most interest because of the sluggish kinetics of the oxygen reduction reaction. Therefore, the cathode is often chosen to be the working electrode (WE). The fuel cell anode is used as the CE/RE with the inherent assumption that polarization of this electrode is small relative to the polarization imposed on the fuel cell cathode, the working electrode. The current densities obtained in the ECSA tests are relatively small and justify this assumption.

The test conditions for *in situ* ECSA evaluation by CV are akin to those used for fuel cell crossover evaluation presented in a the Aug/Sept 2008 issue of *Fuel Cell*⁵. The fuel cell electrode of interest (the WE) is filled with water or slowly purged with a non-reactive gas such as nitrogen, while hydrogen is fed to the other electrode (the CE/RE). See additional comments on the effect of inert gas purge rates below.

The potential of the working electrode is swept at about 20 to 50 mV/s first in the anodic direction to oxidize the adsorbed hydrogen H_{ads} to H^+ and then in the cathodic direction to electrochemically reduce the H^+ back to H_{ads} . Alternating anodic and cathodic currents occur at the electrode. Note that a fuel cell is a driving system whereas the ECSA measurement is a driven system requiring the use of a potentiostat or other controllable power supply.

Results of the CV scan are presented as a voltammogram of current density vs. the working electrode potential (Figure 2). The voltammogram exhibits multiple peaks associated with both the oxidation and reduction reactions. Each peak is indicative of the adsorption onto or desorption from a particular crystal index of platinum, e.g., 100 and 110 indices¹.

Integration of the hydrogen desorption/adsorption peaks that result as a consequence of the forward and reverse scans, respectively, is used to estimate the electrochemically active surface area of the electrocatalyst. The shaded area in Figure 2 represents the charge density q_{Pt} arising from hydrogen adsorption on the Pt catalyst during the reverse sweep.

The baseline current at potentials between 0.4 and 0.6 V is the sum of the capacitive current due to charging/discharging of the electrical double layer (positive on the forward scan and negative on the reverse scan) and the transport limited H_2 crossover current. Non-faradaic or capacitive current arises due to charging/discharging the electrical double layer capacitance of electrode/electrolyte interface. This current involves charge accumulation but not chemical reactions or charge transfer. This current is directly proportional to the scan rate, v (V/s),

$$i_{dl} = C \frac{dE}{dt} = C_{dl} \cdot v \tag{2}$$

where C_{dl} is the specific capacitance of the electrode double layer (Farad/cm²_{electrode}). The electrical charge associated

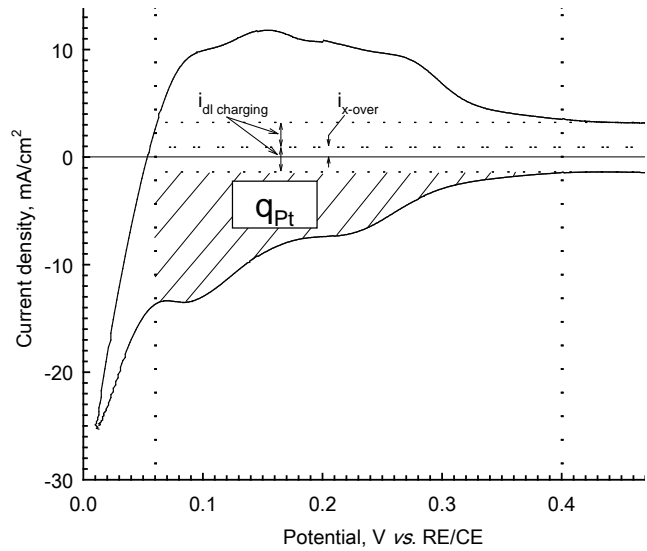


Figure 2. Cyclic voltammogram of a PEMFC catalyst layer highlighting the region of interest. The shaded area is the charge density due to H adsorption during the reverse scan and is used in the ECSA calculation. Conditions as in Figure 1.

with double layer charging and fuel crossover must be accounted for in the analysis to avoid overestimating the charge attributed to the electrocatalytic activity.

Note that the capacitance of the electrode C_{dl} can be determined from the double layer charging current density i_{dl} and Eq. (2). Both the platinum and carbon support contribute to the electrode’s capacitance,

$$C_{dl} = A_{Pt} \cdot C_{dl,Pt}^* + A_{carbon} \cdot C_{dl,carbon}^* \tag{3}$$

where $C_{dl,Pt}^*$ and $C_{dl,carbon}^*$ are the specific double layer capacitance (in F/cm²) for Pt and carbon, respectively, and A_{Pt} and A_{carbon} are the area of platinum and carbon in the electrode (cm²/cm²_{electrode}). The specific double layer capacitance for platinum was reported to be 40 μF/cm²_{Pt}⁶ and for Vulcan XC-72, a common catalyst support material, the value was ~ 8 μF/cm²_{carbon}⁷.

The specific area of platinum A_{Pt} is determined from the previously determined ECSA and the catalyst loading,

$$A_{Pt} (cm_{Pt}^2 / cm_{electrode}^2) = ECSA \times loading \tag{4}$$

From this, the specific area of the carbon catalyst support can be obtained using Eq. (3).

Thus, properties of the catalyst support within the fuel cell electrode can be also be determined from *in situ* CV measurements of the electrochemical surface area of the fuel cell electrodes.

Notes and caveats on hydrogen adsorption for fuel cell electrode catalyst evaluation:

- Both relative humidity (RH) of the gases to which the electrode is exposed, and the electrode temperature

influence the observed ECSA. Fully-saturated or super-saturated ($\geq 100\%$ RH) conditions are generally used.

- The flow rate of nitrogen or other inert gas at the working electrode can significantly influence the shape of the adsorption/desorption curve and calculated ECSA⁸. The artifact was attributed to the rate of mass transfer of H₂ away from the working electrode during the voltage scan. With increasing N₂ purge rate, H₂ is more readily swept from the electrode surface, decreasing the partial pressure of H₂ at the electrode thereby increasing the Nernst potential for hydrogen evolution. All else being equal, conditions that decrease the concentration of H₂ at the working electrode increase the reversible potential for hydrogen evolution. As the potential at which hydrogen evolution begins to occur during the reverse scan increases, the more difficult it is to accurately quantify the hydrogen adsorption from the voltammogram. Low purge gas flow rate ~ 1 sccm/cm² of active area may be preferred.
- Hydrogen adsorption is very suitable for electrocatalysts where the HAD is well defined and not disturbed by other faradaic processes, *e.g.*, Pt, Ir, Rh.
- The HADS method is not suitable for metals such as Ruthenium which exhibit oxygen adsorption-desorption at potentials inside the hydrogen adsorption-desorption region; the contributions can not be separated.
- The HADS method is not suitable for metals, such as Palladium, that absorb H, thus confounding determination of the hydrogen monolayer concentration. Alternative methods such as CO adsorption technique should be used.

Electrochemical surface area experiments are an important diagnostic for fuel cell catalyst, electrode and membrane electrode assembly (MEA) developers and manufacturers. The ECSA should be determined when a new MEA and fuel cell is fabricated as well as periodically during testing as a diagnostic for fuel cell electrode degradation. The experiment should be conducted on membrane electrode assemblies that have been through a break-in procedure to fully activate the electrode. Finally, ECSA measurements are used in RDE studies to ensure that catalyst has not fallen off during the RDE experiments.

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