Modeling of Membrane-Electrode-Assembly Degradation in Proton-Exchange-Membrane Fuel Cells – Local H₂ Starvation and Start–Stop Induced Carbon-Support Corrosion

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1. INTRODUCTION

Hydrogen-powered fuel cell vehicles are perceived as the future of transportation to replace current gasoline-fueled automobiles.¹ Proton-exchange-membrane (PEM) fuel cells, operating at relatively low temperatures with zero emission and high efficiency, are being developed to make automotive fuel cell power systems competitive to current internal-combustion engines. As a durable membrane-electrode-assembly (MEA) is essential for hydrogen-powered fuel cell vehicles to be commercially viable, understanding MEA degradation mechanisms and improving MEA durability are increasingly critical to the successful commercialization of fuel cell vehicles. There are many factors influencing MEA durability.^{1–7} Electrode degradation is one of the most challenging

durability issues for automotive applications that involve dynamic driving cycles with frequent load changes and start–stop events. An electrode is normally composed of platinum (Pt) catalyst supported by high surface-area carbon, such as Vulcan or Ketjen Black (KB). Cathode carbon-support corrosion, which can occur under certain automotive operating conditions, causes electrode structure damage and thus electrode degradation;^{8–13} and therefore it is of great concern to MEA durability.

Figure 1 shows the schematic of a PEM fuel cell where there is an H_2/O_2 front dividing the cell into two portions: one is H_2 -rich and generates electric power as a power source, and the other is H_2 -free and becomes a load driven by the power source. The existence of the H_2/O_2 front results from two scenarios: (a) start–stop events frequently seen in automotive application and (b) local H_2 starvation caused by local blockage of the H_2 fuel supply, e.g., part of anode flow-field is filled with liquid water. As shown in Fig. 1,

Figure 1. The schematic of a PEMFC having the H_2/O_2 front in the anode and major electrochemical reactions considered in the analysis. The H_2/O_2 front divides the fuel cell into the power source and the load. In the load portion, anode flow-field (FF) is occupied by air (or O_2+N_2) in the case of start–stop, while it is filled with liquid water in the case of local H_2 starvation.

normal electrode reactions, HOR (hydrogen oxidation reaction) and ORR (oxygen reduction reaction), occur at the anode and cathode of the H_2 -rich region, respectively. Protons are transported from the anode to the cathode. In the H_2 -free region, however, ORR takes place at the anode, and to get the needed protons it induces OER (oxygen evolution reaction) and COR (carbon oxidation reaction or carbon corrosion) at the cathode, resulting in a so-called *reverse current* of protons,⁸ i.e., protons flowing from the cathode to the anode side. Electrons are transported between H_2 -rich and H_2 -free regions via an internal path at open-circuit voltage (in the case of a normal start–stop process) and via an external path when a load is applied to the fuel cell (in the case of local H_2 starvation). During a start process, hydrogen gas flows into the anode which initially was filled with air. During an extended stop process, air flows into the anode that had been filled with hydrogen gas. In both cases, an H_2 /air-front passes through the anode flow-field, inducing carbon-support corrosion at the cathode where oxygen is present on the corresponding anode side. Start–stop events, where H_2 /air-fronts move through the anode flow-field with residence times in the order of 0.1–1 s, lead to cathode carbon-support corrosion and rapid MEA performance degradation.^{8,10,12} The analogous effect occurs when H_2 access is locally blocked by water droplets or anode diffusion medium flooding, leading to a buildup of N_2 and O_2 via permeation through the membrane from the cathode to the anode side (“crossover”), and thus leading to localized cathode carbon-support corrosion referred to as local H_2 starvation.^{9,11,14}

Much effort has been made to understand carbon-support corrosion mechanisms in recent years. Experiments to simulate start–stop events and local H_2 starvation were conducted with a single cell having two segmented gas flows on the anode as well as with two cells electrically connected in parallel based on the reverse-current mechanism⁸ to observe fuel cell performance decay associated with loss of electrochemically active area and electrode thinning.^{8,10} To quantify the rate of carbon corrosion, CO_2 (and CO) evolution were monitored at the cathode exit,^{15–19} and in-situ electrode potential measurements were made with a reference electrode.^{17,20,21} It has been found that H_2 /air-front-induced voltage degradation during start–stop events can be correlated to the extent of cathode carbon-support weight loss normalized to carbon loading, independent of whether conventional or graphitized carbon-supports are used.^{11,12}

Consequently, since graphitized carbon-supports have lower carbon corrosion rates, the use of cathode catalysts with graphitized supports significantly reduces H_2 /air-front start–stop damage.^{12,22} Furthermore, if the ORR activity of the anode electrode is reduced by lowering anode Pt loading, H_2 /air-front start–stop degradation is decreased.^{22,23}

Mathematical models have been developed to understand experimental observations and to further explore mitigation methods.^{8,12,14,15,24–32} The complexity of the models varies with model application and physics incorporated. For example, a one-dimensional model for the electrolyte potential profile along the gas-flow direction was developed to explain the reverse-current mechanism.⁸ Hydrogen and oxygen transport were incorporated to describe how cathode carbon corrosion can be induced by a maldistribution of H_2 across the anode.²⁴ A two-dimensional, steady-state model for the electrolyte potential distribution along the gas-flow direction and across MEA thickness was developed to investigate the effect of cell voltage, ionomer proton conductivity, H_2 -starved region size, carbon corrosion kinetics, and oxygen permeability through the membrane on the carbon corrosion rate.²⁵ Later, the model was extended to simulate a transient process with quasi-steady-state assumption and investigate the influence of MEA design parameters, such as ORR exchange current density on the anode and the thickness of the membrane.^{26,27} CFD (Computational-Fluid-Dynamics) based models have also been developed with electrode kinetics coupled with transport for two-dimensional, steady-state simulation,^{28,29} and two- and three-dimensional, transient simulations.³⁰ Most recently, attempts were made to couple carbon-support corrosion with voltage degradation via multi-scale modeling.^{31,32}

In this chapter, we will review the fundamental models that we developed to predict cathode carbon-support corrosion induced by local H_2 starvation and start–stop in a PEM fuel cell, and show how we used them to understand experiments and provide guidelines for developing strategies to mitigate carbon corrosion. We will discuss the kinetic model,¹² coupled kinetic and transport model,¹⁴ and pseudo-capacitance model¹⁵ sequentially in the three sections that follow. Given the measured electrode kinetics for the electrochemical reactions appearing in Fig. 1, we will describe a model, compare the model results with available experimental data, and then present

the implications of the model predictions. Finally, we will summarize the applicability and usefulness of each model and provide an outlook on further model improvement for better fundamental understanding of MEA degradation associated with carbon-support corrosion.

2. KINETIC MODEL

2.1. Electrode Kinetics

A kinetic model is built based on the electrode kinetics of all electrochemical reactions involved in Fig. 1. We have measured the kinetics of HOR³³ and ORR³⁴ for the power source, as well as the kinetics of OER³⁵ and COR¹² for the load. The electrode reaction currents are governed by

$$i_{\text{HOR}} = a_{\text{Pt}} L_{\text{Pt}} i_{o,\text{HOR}}(T, p_{\text{H}_2}) \frac{2F}{RT} \eta_{\text{HOR}} \quad (1)$$

$$i_{\text{ORR}} = a_{\text{Pt}} L_{\text{Pt}} i_{o,\text{ORR}}(T, p_{\text{O}_2}) \exp\left(-\frac{\alpha_{\text{c,ORR}} F}{RT} \eta_{\text{ORR}}\right) \quad (2)$$

$$i_{\text{OER}} = a_{\text{Pt}} L_{\text{Pt}} i_{o,\text{OER}}(T, p_{\text{H}_2\text{O}}) \exp\left(\frac{\alpha_{a,\text{OER}} F}{RT} \eta_{\text{OER}}\right) \quad (3)$$

and

$$i_{\text{COR}} = a_{\text{C}} L_{\text{C}} (1 - \theta)^m i_{o,\text{COR}}(T, p_{\text{H}_2\text{O}}) \exp\left(\frac{\alpha_{a,\text{COR}} F}{RT} \eta_{\text{COR}}\right) \quad (4)$$

where a and L are the electrochemically active surface area (in cm^2/mg) and loading of an ingredient in an electrode (in mg/cm^2), with subscripts Pt and C representing platinum and carbon, respectively. L_{C} relates to L_{Pt} via $r_{\text{Pt/C}}$, the weight ratio of platinum over carbon used to fabricate C-supported Pt catalyst. θ is the mass fraction of carbon support that has been lost. R is the universal gas constant (8.314 J/mol/K), F is the Faraday constant (96487 C/eq), and T is temperature (in Kelvin). The reaction-specific exchange current density, $i_{o,j(T,p_i)}$ in units of $\text{A}/\text{cm}^2_{\text{Pt or C}}$, is dependent on temperature and gaseous reactant partial pressure:

$$i_{o,j(T,p_i)} = i_{o,j}^{\text{ref}} \cdot \left(\frac{p_i}{p_i^{\text{ref}}} \right)^{\gamma_i} \exp \left[-\frac{E_j^{\text{rev}}}{RT} \left(1 - \frac{T}{T^{\text{ref}}} \right) \right] \quad (5)$$

where $i_{o,j}^{\text{ref}}$ is the specific exchange current density normalized to the reference gaseous reactant partial pressure (p_i^{ref}) of 101.3 kPa and a reference temperature (T^{ref}) of 353 K (80 °C), γ_i is the apparent reaction order of species i in an electrode reaction, and E_j^{rev} is the activation energy of the electrode reaction j at the reversible cell potential (zero overpotential).

In Eqs. (1–4), the surface overpotential (driving force for an electrode reaction) is defined as

$$\eta_j = \phi_s - \phi_e - E_{j(T)}^o \quad (6)$$

where j = HOR, ORR, OER, and COR. ϕ stands for the electrical potential of a phase, with subscript s and e representing the electron-conducting solid phase and the proton-conducting electrolyte (or ionomer) phase, respectively. $E_{j(T)}^o$ is the standard equilibrium potential of an electrode reaction versus RHE (reversible hydrogen electrode).³⁶

$$E_{j(T)}^o = E_{j(298.15\text{K})}^o + \frac{dE_j^o}{dT}(T - 298.15) \quad (7)$$

As COR and OER occur simultaneously in the cathode, their kinetics are particularly important in evaluating carbon-support corrosion. The kinetics of OER is material-specific, dependent on catalyst composition and electrode fabrication.^{35,37–39} A number of OER kinetics studies were done on Pt metal electrodes.^{37–39} However, there is a lack of OER kinetics data on electrodes made of Pt nano-particles dispersed on carbon supports. Figure 2 shows the measured OER current density with respect to the overpotential defined by Eq. (6).³⁵ The O₂ concentration was measured at the exit of a 50-cm² cell using a gas chromatograph (GC). The O₂ evolution rate (= O₂ concentration × cathode flow rate) was then converted to the OER current density, assuming 4e[−]/O₂ molecule. Diluted H₂ (10%) and a thicker membrane (50 μm) were used in the measurement to minimize H₂ crossover from anode to cathode, because H₂ would react with O₂ evolved at the cathode and incur inaccuracy in the measured OER current density. Figure 2 indicates that the OER

Figure 2. Oxygen evolution reaction current density (in units of A/g_{Pt}) with respect to the overpotential applied to the cathode electrode. The OER current density is based on the measured O₂ concentration at the exit of a 50-cm² cell using a GC, assuming 4e⁻/O₂ molecule. The cell is operating with 10% H₂/He (150 kPa_{abs}, varying T and RH) at various potentiostatic conditions.

current density follows the Tafel equation and is a strong function of temperature. The OER kinetic parameter values were determined by fitting the OER current densities to Eq. (3).³⁵

The carbon corrosion rate depends on the potential, temperature, and time for a specific carbon material.¹ Figure 3 displays carbon corrosion rate versus carbon weight loss based on the measured CO₂ concentration at the exit of a 50-cm² cell using a GC when the cell was held at 1.2 V versus RHE.¹² It shows that the corrosion rate of the conventional carbon support (KB) decreases with time (reflected by the carbon weight loss), whereas the corrosion rate of the graphitized carbon support (Gr-KB) remains nearly constant. The time dependence of the carbon-support corrosion rate is most likely related to the inhomogeneous graphitization of commonly used carbon supports, which generally consist of primary particles with diminishing graphitic order toward the particle center.²² As depicted in Fig. 3, a carbon particle is made up of an amorphous core with a graphene-like shell.⁴⁰ Since the corrosion

Figure 3. Carbon corrosion rate versus carbon weight loss for both conventional and graphitized KB-supported Pt catalysts. The carbon corrosion rate (in units of A/g_C) is based on the measured CO_2 concentration at the exit of a 50 cm^2 cell using a GC, assuming $4e^-/CO_2$ molecule. The carbon weight loss is obtained by integrating the measured CO_2 evolution rate over time. The cell is operating on neat H_2/N_2 (95 °C, 80% RH_{in} , and 120 kPa_{abs}) with potential held at 1.2 Volts versus RHE.

resistance of carbon within a graphitic plane is approximately one to two orders of magnitude higher than that of carbon along the edges of graphitic planes,⁴¹ the corrosion of conventional carbon supports like KB should begin in the center region of the primary carbon-black particles (high density of graphitic plane edge sites and/or amorphous carbon), and progress over time toward the more graphene-like (and thus more corrosion resistant) shell region that has a lower density of graphitic plane edge sites.²² The most recent electron microscopy observations of the centered-hollowed carbon particles and interconnected voids concluded that carbon corrosion indeed takes place in an inside-out mode, with the carbon aggregate, rather than the carbon primary particle, as a basic corrosion unit.¹³ In Eq. (4), the time dependence is taken into account via the index m by fitting to the measured carbon corrosion rates.

All thermodynamic and kinetic parameter values needed in calculating the electrode reaction current densities are listed in Table 1.

Table 1
Thermodynamic and Kinetic Parameter Values. Values of
Standard Electrode Potential (at 25 °C) and Exchange Current
Density (at 80 °C) are Referenced to 101.3 kPa Gaseous
Reactant Partial Pressure.

Parameter	Unit	Value
<i>HOR</i>		
Standard electrode potential	V	0
Temperature coefficient	V/K	0
Exchange current density	A/cm ² _{Pt}	0.3
Activation energy at zero overpotential	J/mol	10×10 ³
Hydrogen reaction order		1
<i>ORR</i>		
Standard electrode potential	V	1.2291
Temperature coefficient	V/K	−0.8456×10 ^{−3}
Exchange current density	A/cm ² _{Pt}	2.47×10 ^{−8}
Activation energy at zero overpotential	J/mol	67×10 ³
Cathodic transfer coefficient		1
Oxygen reaction order		0.79
<i>OER</i>		
Standard electrode potential	V	1.2291
Temperature coefficient	V/K	−0.8456×10 ^{−3}
Exchange current density	A/cm ² _{Pt}	1.89×10 ^{−9}
Activation energy at zero overpotential	J/mol	38×10 ³
Anodic transfer coefficient		0.65
Water vapor reaction order		0.88
<i>COR</i>		
		Vulcan/Gr-Vulcan
Standard electrode potential	V	0.2073
Temperature coefficient	V/K	−0.8530×10 ^{−3}
Exchange current density	A/cm ² _C	1.03×10 ^{−18} /2.17×10 ^{−19}
Activation energy at zero overpotential	J/mol	134×10 ³ /140×10 ³
Anodic transfer coefficient		0.67/0.65
Index for carbon weight loss dependence		10.4/0

The standard electrode potential and its temperature coefficient are found in the literature.³⁶ Kinetic parameter values were measured in-house for HOR,³³ ORR,³⁴ OER,³⁵ and COR.^{12,22} Table 2 gives cell component materials and transport properties. The membrane and electrode proton conductivity in Table 2 are based on the measured membrane and electrode resistance,^{42,43} which is a strong function of relative humidity (RH). In what follows next, we will describe the

Table 2
Cell Component Materials Properties.

Parameter	Unit	Value/equation
<i>Geometric</i>		
Membrane thickness	cm	18×10^{-4}
Electrode thickness ($r_{\text{Pt/C}} = 1$)	$\text{cm}/(\text{mg}_{\text{Pt}}/\text{cm}^2)$	30×10^{-4}
Electrode Pt loading (anode/cathode)	$\text{mg}_{\text{Pt}}/\text{cm}^2$	0.4/0.4
DM thickness (under compression)	cm	150×10^{-4}
Electrode porosity		0.5
Electrode pore diameter	cm	50×10^{-7}
DM porosity (under compression)		0.6
DM tortuosity		2.4
Specific Pt surface area	$\text{cm}^2_{\text{Pt}}/\text{mg}_{\text{Pt}}$	600
Specific carbon surface area (Vulcan/Gr-Vulcan)	$\text{cm}^2_{\text{C}}/\text{mg}_{\text{C}}$	2400/800
<i>Transport</i>		
Membrane proton conductivity at 80 °C	S/cm	$1.84 \times 10^{-5} \times (\text{RH}\%)^{1.84}$
Electrode proton conductivity at 80 °C	S/cm	$4.66 \times 10^{-8} \times (\text{RH}\%)^{2.84}$
Activation energy for proton conduction	J/mol	6×10^3
Electrode electrical conductivity	S/cm	1
DM electrical conductivity	S/cm	100
FF electrical conductivity	S/cm	10^4
DM/FF electrical contact resistance	$\Omega \text{ cm}^2$	0.03
Electrode permeability	cm^2	7×10^{-14}
DM permeability	cm^2	10^{-8}

kinetic models for local H_2 starvation and start–stop, respectively, and use the models to evaluate carbon corrosion rate and compare the model results with available experimental data. Furthermore, we will discuss the implications of the model predictions.

2.2. Local H_2 Starvation Model

In the fully developed H_2 starvation region, where H_2 is completely depleted, the cathode electrode potential reaches its maximum value as determined by the mixed potential of all electrochemical reactions involved at the cathode, namely, COR and OER. The reaction current therein is determined by O_2 crossover (i_{x,O_2}) from cathode through membrane to anode, where only ORR takes place in the absence of H_2 . Charge balance yields

$$i_{x,O_2} = i_{COR,cath} + i_{OER,cath} \quad (8)$$

Equation (8) states the fact that the sum of carbon corrosion current ($i_{CO_2} = i_{COR,cath}$) and oxygen evolution current ($i_{O_2} = i_{OER,cath}$) on the cathode must be equal to the oxygen reduction current on the anode determined by the O_2 crossover rate:

$$i_{x,O_2} = 4FK_{O_2}^m \frac{p_{O_2,cath}}{\delta_{mem}} \quad (9)$$

Here, the gas permeability through the membrane is calculated by the semiempirical correlation⁴⁴

$$K^m = k^{dry} \exp\left(-\frac{E^{dry}}{RT}\right) + \nu_{H_2O} k^{wet} \exp\left(-\frac{E^{wet}}{RT}\right) \quad (10)$$

where ν_{H_2O} is the volume fraction of water, which is dependent on membrane equivalent weight, density (at dry state), and water content. k and E are the Arrhenius pre-exponential and activation energy (with superscripts dry and wet denoting the phase state). The values of the various constants can be found in the reference⁴⁴ for each species of interest.

Figure 4 plots polarization curves of COR and OER, together with O_2 crossover current density that controls the total amount of current at the cathode based on the local H_2 starvation model, Eq. (8). The cell operates at 80 °C, 150 kPa_{abs}, 100% RH_{in}, and 2/2 stoichiometric flows using neat H_2 /air. Under these conditions, the O_2 crossover current through the membrane is 0.48 mA/cm² based on measured membrane permeability.⁴⁴ Figure 4 illustrates that the relative rate of carbon corrosion to oxygen evolution has significant implications for mitigating carbon-support corrosion: either making the carbon-support more corrosion-resistant via graphitization or enhancing the oxygen evolution reaction via addition of O_2 evolution catalysts can greatly reduce carbon-support loss, since in these cases the O_2 evolution reaction will more effectively balance the permeation-limited O_2 reduction reaction on the anode.

The kinetic model described by Eq. (8) can be used to evaluate the material impact on the carbon corrosion rate. As shown for 50% Pt/Vulcan in Fig. 4 and Table 3 (first row), its carbon corrosion rate is essentially equal to the O_2 crossover current. Since the

Figure 4. Polarization curves of carbon corrosion and oxygen evolution reactions based on measured carbon corrosion kinetics for Pt/Vulcan and Pt/Graphitized-Vulcan and oxygen evolution kinetics for Pt/C catalysts. The upper horizontal dotted line denotes a current density equivalent to oxygen crossover through membrane from cathode to anode.

Table 3
Catalyst, Catalyst-Support, and Membrane Material Impact on Maximum Catalyst-Support Corrosion Rate Under Fully Developed H₂ Starvation Conditions. Here, *Advanced-Support* is a Hypothetical Support with a 30-Fold Lower Corrosion Rate than Graphitized Vulcan Carbon and *Membrane-X* Refers to a Hypothetical Membrane with a 10-Fold Lower O₂ Permeability.

Catalyst	Membrane	$i_{\text{CO}_2, \text{max}}$ [mA/cm ²]	Gain
50% Pt/Vulcan	PFSA (18 μm)	46×10^{-2}	1×
50% Pt/Gr-Vulcan	PFSA (18 μm)	26×10^{-2}	1.8×
50% Pt/advanced-support	PFSA (18 μm)	1.8×10^{-2}	26×
50% Pt/Gr-Vulcan + 10× OER	PFSA (18 μm)	4.8×10^{-2}	9.5×
50% Pt/Vulcan	<i>Membrane-X</i>	4.6×10^{-2}	10×

electrode performance drops rapidly once $\approx 10\%$ wt. of the carbon-support is corroded,^{6,11} it takes only ≈ 3000 s under these conditions to destroy the electrode. As shown in Fig. 4 and Table 3 (second row), the carbon corrosion rate is reduced to $\approx 57\%$ of O_2 crossover current by the use of graphitized Vulcan carbon-support, indicating the importance of the relative rate of carbon corrosion to oxygen evolution. Furthermore, if one was able to develop a high surface area catalyst support with 30-fold higher corrosion resistance than graphitized Vulcan (Table 3, third row), the catalyst-support corrosion damage would be reduced by ≈ 26 -fold (possible candidates are, e.g., boron-doped diamond supports^{45,46}). An alternative route toward improved carbon-support corrosion stability during local H_2 starvation is the addition of a more effective O_2 evolution catalyst to the cathode electrode, analogous to what was proposed previously in the context of carbon-support corrosion damage during cell reversal.^{47,48} If oxygen evolution kinetics are enhanced by a factor of 10 over Pt/C (e.g., by means of addition of IrO_2 and RuO_2 catalysts,⁴⁸ etc.), the carbon corrosion rate would be reduced by a factor of 10 if graphitized Vulcan is used as catalyst-support (Table 3, fourth row). Finally, as the total current is controlled by the O_2 crossover, the use of a hypothetical membrane with a 10-fold lower O_2 permeability would result in a proportionally lower carbon corrosion rate (Table 3, fifth row).

2.3. Start–Stop Model

Considering that at a time t , the H_2 /air-front, which divides the fuel cell into the power source (the H_2 /air cell) and the load (the air/air cell), is located at x (normalized anode channel length), conservation of charge yields:

$$i_{\text{Power}} = [i_{\text{HOR,an}} = i_{\text{ORR,cath}}]_{H_2 - \text{rich gas/Air}} \quad (11)$$

for the power source,

$$i_{\text{Load}} = [i_{\text{ORR,an}} = i_{\text{COR,cath}} + i_{\text{OER,cath}}]_{H_2 - \text{free gas/Air}} \quad (12)$$

for the load, and

$$i_{\text{Power}}x = i_{\text{Load}}(1 - x) \quad (13)$$

as the equal amount of current flows through both H_2 /air and air/air cells.

Equations (11), (12), and (13) can be solved for three unknowns $\phi_{e,Power}$, $\phi_{e,Load}$, and $\phi_{s,cath}$ with reference to $\phi_{s,an} = 0$ (set arbitrarily) when the difference in electrolyte phase potential between anode and cathode electrodes is negligible, which is a good assumption at a very low current density. However, anode and cathode electrolyte phase potentials can be differentiated by adding two more equations, namely

$$\begin{cases} \phi_{e,cath} = \phi_{e,an} + i_{Power}R_{H^+} & \text{for the power source portion} \\ \phi_{e,cath} = \phi_{e,an} - i_{Load}R_{H^+} & \text{for the load portion} \end{cases} \quad (14)$$

where the protonic resistance is estimated by^{42,43}

$$R_{H^+} \approx R_{H^+, mem} + R_{H^+, cath}/3 \quad (15)$$

which is the sum of membrane resistance and the effective cathode electrode resistance to proton transport.

Figure 5 gives a graphic solution of the start–stop model with the H_2/O_2 front passing through the center of the anode flow-field, representative of the average carbon corrosion rate. The 50-cm² cell undergoes start–stop cycles at 80 °C, 66% RH_{in}, and 150 kPa_{abs} with a residence time of 1.5 s based on anode void volume (including flow-field and diffusion medium). Figure 5 plots polarization curves for both the H_2 /air cell (power source) and the air/air cell (load). The intercept point gives the balanced current density ($i_{OER} + i_{COR}$) that flows through the load and therefore causes carbon corrosion accompanied by oxygen evolution. For the base case (0.40 mg_{Pt}/cm² on Vulcan), the balanced current density is 0.125 A/cm², nearly all of which goes to carbon corrosion. In case (a), replacing Vulcan with Gr-Vulcan significantly increases the resistance to COR and reduces the balanced current density to 0.040 A/cm², more than 1/3 of which goes to oxygen evolution reaction. In case (b), lowering anode Pt loading to 0.05 mg_{Pt}/cm² on Vulcan increases the resistance of the load to ORR and thus decreases the balanced current density to 0.072 A/cm², but only 3% of it is taken by oxygen evolution. The modeled gain (defined as the ratio of the base case carbon corrosion current density over the carbon corrosion current density

Figure 5. Graph illustrating reduction of cathode carbon corrosion during start-stop with (a) corrosion-resistant carbon support (Gr-Vulcan) and (b) lower anode catalyst loading ($0.05 \text{ mgPt}/\text{cm}^2$). The base case is Vulcan and $0.40 \text{ mgPt}/\text{cm}^2$ anode loading.

of the case of interest) agrees well with the measured start-stop degradation rates at $1.2 \text{ A}/\text{cm}^2$, as shown in Table 4.

Carbon corrosion current density can be further reduced by controlling the cell voltage at a low level during the start-stop process.^{25,27} Neglecting i_{OER} , Eq. (12) is simplified to

Table 4
Measured Start-Stop Degradation Rates at $1.2 \text{ A}/\text{cm}^2$
Normalized to H_2/O_2 Front Residence Time on a 50 cm^2 Cell at
 80°C , $66\% \text{ RH}_{\text{in}}$, $150 \text{ kPa}_{\text{abs}}$, Compared to the Modeled
 $i_{\text{CO}_2, \text{base}}/i_{\text{CO}_2}$ from Fig. 5.

Anode Pt loading (mgPt/cm^2)	Carbon support	Degradation rate ($\text{mV}/\text{cycle}/\text{s}$)	Gain	
			Experiment	Model
0.40	Vulcan	1.3	$1\times$	$1\times$
0.40	Gr-Vulcan	0.25	$5.2\times$	$4.9\times$
0.05	Vulcan	0.75	$1.7\times$	$1.8\times$

$$i_{\text{ORR,an}} = i_{\text{COR,cath}} \quad (16)$$

Using Eqs. (2), (4), and (6) in Eq. (16), one finds the surface overpotential that drives COR at the cathode²⁷ is

$$\eta_{\text{COR,cath}} = \frac{\alpha_{\text{c,ORR}}}{\alpha_{\text{a,COR}} + \alpha_{\text{c,ORR}}} (\phi_{\text{s,cath}} - \phi_{\text{s,an}}) + \frac{RT}{F(\alpha_{\text{a,COR}} + \alpha_{\text{c,ORR}})} \left[\ln \left(\frac{a_{\text{Pt}} L_{\text{Pt}} i_{\text{o,ORR}}}{a_{\text{C}} L_{\text{C}} (1 - \theta)^m i_{\text{o,COR}}} \right) + \frac{\alpha_{\text{c,ORR}} F}{RT} (E_{\text{ORR}}^o - E_{\text{COR}}^o) \right] \quad (17)$$

With the given MEA configuration and operating condition, the second term on the right hand side of Eq. (17) is constant. Therefore, η_{COR} is linearly proportional to the IR-corrected cell voltage ($\phi_{\text{s,cath}} - \phi_{\text{s,an}}$), meaning that i_{COR} can be significantly reduced if the cell potential is controlled to a low enough value. Physically, the current generated from the H₂-rich portion of the fuel cell is forced to be applied to an external load when controlling the cell potential, thus reducing the current flowing through the H₂-free portion of the cell and causing less carbon-support corrosion.

3. COUPLED KINETIC AND TRANSPORT MODEL

3.1. Model Description

A two-dimensional, electrochemical, and transport-coupled transient fuel cell model is developed based on the laws of conservation of species and charge¹⁴:

$$\frac{\partial(\varepsilon c_i)}{\partial t} + \nabla \cdot (c_i \mathbf{v}) = \nabla \cdot (D_i \nabla c_i) + \frac{s_i \dot{I}_j}{n_j F \delta_{\text{CL}}} \quad (18)$$

$$\nabla \cdot (\sigma \nabla \phi_s) - \sum_j i_j / \delta_{\text{CL}} = 0 \quad (19)$$

$$\nabla(\kappa \nabla \phi_e) + \sum_j i_j / \delta_{\text{CL}} = 0 \quad (20)$$

where c_i is the molar concentration of species i ($i = \text{H}_2$, O_2 , and N_2), ε is the porosity of a porous medium such as DM (diffusion medium) and CL (catalyst layer), D_i is the effective diffusivity of species i , σ is the effective electronic conductivity of the solid phase, κ is the effective proton conductivity of the electrolyte phase, δ_{CL} is the thickness of an electrode, s_i is the stoichiometry of species i in reaction j , and n_j is the number of electrons involved in the electrode reaction. We assume that Darcy's law applies to the gas phase in porous media for the superficial gas velocity:

$$\mathbf{v} = -\frac{K^g}{\mu} \nabla p \quad (21)$$

where K^g is the permeability of a porous medium and μ is the gas viscosity. The gas pressure is calculated based on ideal gas law and the assumption of equilibrium water vapor pressure:

$$p = RT \sum_i c_i + p_{\text{H}_2\text{O}}^{\text{sat}}(T) \quad (22)$$

with the saturated water vapor pressure as a function of T in degree Celsius

$$\log p_{\text{H}_2\text{O}}^{\text{sat}}(\text{atm}) = -2.1794 + 2.9535 \times 10^{-2}T - 9.1838 \times 10^{-5}T^2 + 1.4454 \times 10^{-7}T^3 \quad (23)$$

The permeability of an electrode can be estimated from the electrode porosity (ε) and pore diameter (d) by the Kozeny–Carmen relation

$$K^g = \frac{\varepsilon^3 d^2}{180(1 - \varepsilon)^2} \quad (24)$$

The typical value of DM permeability varies from 1 to 10 Darcy (1 Darcy $\equiv 10^{-8} \text{ cm}^2$) from Gurley measurement.

The gas viscosity can be calculated by the semiempirical formula of Wilke⁴⁹:

$$\mu_{\text{mix}} = \sum_{i=1}^n \frac{x_i \mu_i}{\sum_j x_j \Phi_{ij}} \quad (25)$$

in which the dimensionless quantities Φ_{ij} are

$$\Phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j} \right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2 \quad (26)$$

Here x_i and M_i are the mole fraction and molecular weight of species i in the gas mixture of n species and μ_i is the viscosity of pure species i at the system temperature and pressure.

The molecular diffusion coefficient of species i in a multi-component mixture can be calculated by the Wilke formula:⁵⁰

$$D_{i,\text{mix}} = \frac{1 - x_i}{\sum_{j=1, j \neq i}^n x_j / D_{i,j}} \quad (27)$$

Here $D_{i,j}$ is the binary diffusion coefficient. In DM, the effective diffusivity of species i is calculated by

$$D_i = D_{i,\text{mix}} \frac{\varepsilon}{\tau} \quad (28)$$

in which the effect of porosity (ε) and tortuosity (τ) is accounted for. In an electrode with small pores, Knudsen diffusion (molecule-to-wall collision) contributes to the effective diffusivity of species i :

$$D_i = \left(\frac{1}{D_{K,i}} + \frac{1}{D_{i,\text{mix}}} \right)^{-1} \varepsilon^{1.5} \quad (29)$$

where the Knudsen diffusion coefficient is calculated based on pore diameter (d in cm), species molecular weight (M_i in g/mole), and system temperature (T in Kelvin) by

$$D_{K,i} = 4850d \left(\frac{T}{M_i} \right)^{1/2} \quad (30)$$

Notice that the Bruggeman correlation is employed for tortuosity of the electrode in Eq. (29). The porosity-to-tortuosity of DM in Eq. (28) can be obtained by the limiting current method.^{51,52}

In the membrane, the effective diffusivity of species i is calculated by

$$D_i = K_i^m RT \times 10^3 \quad (31)$$

where the gas permeability through membrane is calculated by Eq. (10).

Equations (18–20) are discretized by the control volume method⁵³ and solved numerically to obtain distributions of species (H_2 , O_2 , and N_2) concentration, phase potential (solid and electrolyte), and the current resulting from each electrode reaction, in particular, carbon corrosion and oxygen evolution currents at the cathode catalyst layer, with the following initial and boundary conditions:

$$\begin{aligned} \text{At} \quad & t = 0, \\ & c_i = c_i^o \end{aligned} \quad (32)$$

$$\text{At} \quad t > 0,$$

$$c_i = c_{i,\text{in}} \quad \text{at inlets based on gas compositions,} \quad (33a)$$

$$\frac{dc_i}{dx} = 0 \quad \text{at outlets,} \quad (33b)$$

$$-\sigma \frac{\partial \phi_s}{\partial y} = i_{\text{app}} \quad \text{at outer boundaries of flow-fields,} \quad (33c)$$

$$\frac{\partial \phi_e}{\partial y} = 0 \quad \text{at CL/DM interfaces,} \quad (33d)$$

$$\mathbf{v} = \mathbf{v}_{\text{in}} \quad \text{at inlets based on given flow rates,} \quad (33e)$$

The model applies to both Cartesian and cylindrical coordinates. The x -coordinate denotes in-plane direction and the y -coordinate refers to thru-plane direction.

3.2. Local H_2 Starvation Simulation

We use the coupled kinetic and transport model to predict when local H_2 starvation occurs and how it affects carbon corrosion rate.

Figure 6 shows in a cylindrical coordinate (radial/thru-plane) how H_2 depletes and N_2 pressure builds up with time. At the center of the H_2 -starved region, the N_2 pressure becomes higher than 80 kPa_{abs} after 1 s. The radius of this N_2 bubble grows to 7 mm after 10 s and covers 80% of the liquid-water-blocked region at 100 s (near steady-state). The H_2 pressure drops quickly to zero at the edge of the N_2 bubble, within which the cathode potential rises sharply, and the carbon corrosion rate starts to increase, as shown in Fig. 7. Conventional DM has a value of permeability ranging from 1 to 10 Darcy. There is no impact of DM permeability within its realistic range.¹⁴ N_2 crossover through the membrane results in N_2 pressure build-up in the H_2 -starved anode region. As a result, convective

Figure 6. H_2 depletion and N_2 bubble buildup at the center of H_2 -starved region resulting from H_2O -filled/blocked channels with a radius of 20 mm as shown above on the plot. The cell operates on neat H_2 /air at $\approx 1.5\text{ A/cm}^2$ ($80\text{ }^\circ\text{C}$, $150\text{ kPa}_{\text{abs}}$, $100\%\text{ RH}_{\text{in}}$). There are only H_2 and water vapor in the anode and DM at $t = 0$.

Figure 7. Evolution of cathode potential (defined as $\phi_s - \phi_e$ at cathode electrode) and carbon corrosion current distributions corresponding to H_2 depletion and N_2 bubble buildup as shown in Fig. 6.

flows become insignificant at steady-state, rendering both potential and current distributions that are solely determined by diffusion.

Figure 8 compares the predicted residual carbon support in the cathode with measured electrode thinning after a controlled local H_2 starvation test.⁵⁴ Above the plot a schematic is shown. The anode flow-field is partially blocked, creating a region of 60 mm in width where there is no channel. The cathode electrode thickness was measured at the four locations marked by dashed lines after a 13-h run at 1.2 A/cm². The model simulation was carried out on a Cartesian coordinate (two-dimensional across the blocked region – through cell thickness). Figure 8 shows that the modeled residual carbon support agrees qualitatively with the measured electrode thickness across the blocked region.

Information on the length scales beyond which H_2 depletes and carbon corrosion takes place is valuable for developing system mitigation strategies. Figure 9 shows that the length scale for H_2 to deplete is independent of the length scale of the H_2 -starved region, while the larger the H_2 -starved region, the higher the carbon corrosion at the center of the H_2 -starved region. The insert in Fig. 9 (top) illustrates that the length scale is determined by letting $i_{HOR} - i_{x,O_2}$

Figure 8. Comparison of the predicted residual carbon support in the cathode with the measured cathode thickness after 13 h run at 1.2 A/cm^2 (70% H_2 /air counter-flow, 80°C , $150 \text{ kPa}_{\text{abs}}$, 40%/60% RH_{in}) with partially filled flow channels as shown above the plot.

be zero. Figure 9 (bottom) shows that a radial length scale of more than 20 mm (40 mm in diameter) is required to allow for a fully developed H_2 starvation region, indicating that a large number of adjacent channels need to be filled with water or blocked by water droplets. The cathode potential (reflected by normalized carbon corrosion current density) is substantially lower in the region where a local H_2 starvation region is not fully developed.

The length scale for H_2 to deplete depends strongly on applied current density, as shown in Fig. 10. The length scale increases as current density decreases. As a result, an H_2 -starved region is more likely to be fully developed at a high current density, whereas it tends to be underdeveloped at a low current density. Figure 11 gives the length scales beyond which H_2 would deplete, and the carbon

Figure 9. Top: HOR (less O_2 crossover) current density distribution with respect to length scales of a local H_2 -starved region determines where H_2 depletes. Bottom: carbon corrosion current distribution with respect to length scales of a local H_2 -starved region shows how a fully starved region develops. The cell operates on neat H_2 /air at $\approx 1.5 \text{ A/cm}^2$ (80°C , 150 kPa_{abs} , $100\% \text{ RH}_{in}$).

corrosion current density would exceed 10 and 50%, respectively, of i_{x,O_2} at the center of the H_2 -starved region, with respect to applied current density. It shows that the radial length scale for 10% i_{x,O_2} carbon corrosion current density is 6 mm larger than the radial length scale for H_2 depletion.

Figure 10. The scale of H₂ depletion (top) and corresponding carbon corrosion current distribution (bottom) depends on the applied current density. The cell operates on neat H₂/air (80 °C, 150 kPa_{abs}, 100% RH_{in}) with a local H₂-starved region of 20 mm in radius.

Figure 12 shows the time scales at which the carbon corrosion current reaches 50% of its maximum value at the center of the H₂-starved region. Local H₂ starvation takes place within ~2–40 s of anode channel flooding/blocking at a high current density,

Figure 11. Calculated length scales with respect to applied current density for a cell operating on neat H₂/air (80 °C, 150 kPa_{abs}, 100% RH_{in}). The solid line represents the length scale beyond which H₂ depletes. The long and short dashed lines denote the length scales beyond which the maximum carbon corrosion current density would exceed 10% and 50% of O₂ crossover current density, respectively.

depending on the length scale of the blocked flow-field region. It takes longer for a shorter length scale of the flooded/blocked area. The time scale correlates closely to the N₂ pressure buildup, which in turn depends on the membrane's N₂ permeability. Longer times to reach steady-state are required for membranes with lower N₂ permeability. Figure 12 also shows that the time scales are strongly dependent on the applied current density.

Diluting H₂ with N₂ has a drastic impact on length and time scales. Figure 13 shows the comparisons between 100% H₂ and 70% H₂ diluted with 30% N₂. When H₂ is consumed in the blocked area, a vacuum is created, inducing convective flow. When there is N₂ in the anode gas stream, such convection helps to build up N₂ pressure much more quickly than N₂ permeation from cathode to anode. Figure 13(a) shows that the length scale for H₂ depletion decreases greatly with dilution of H₂. More strikingly, the H₂-starved region becomes fully developed even at 0.05 A/cm², which yields only 1% i_{x,O_2} with 100% H₂. Figure 13(b) shows that the time scales

(a)

(b)

Figure 12. Evolution of the maximum carbon corrosion current density at the center of a local H_2 -starved region and calculated time constants (defined as the time to 50% of the maximum carbon corrosion current density) with respect to length scales of a local H_2 -starved region for a cell operating on neat H_2 /air (80 °C, 150 kPa_{abs}, 100% RH_{in}).

Figure 13. Effect of N_2 dilution in the anode on length scale and time constant for carbon corrosion in a local H_2 -starved region of 20 mm in radius. The cell operates on neat (100%) and N_2 -diluted (70%) H_2 /air (80 °C, 150 kPa_{abs}, 100% RH_{in}).

are significantly reduced to less than 2 s for both 1.50 and 0.05 A/cm² cases. This shows the importance of keeping the concentration of N_2 in the anode at a low level to mitigate cathode carbon corrosion.

3.3. Start–Stop Simulation

The two-dimensional, coupled kinetic and transport model can also be used to simulate start–stop processes. Figure 14 plots cathode potential and carbon corrosion current distribution at three instants when the H_2/O_2 front passes through 10, 50, and 90% of anode flow path during the start process. As H_2 displaces air in the anode flow-field, the size of the power source increases and the load size decreases accordingly. The balanced current density becomes larger, causing higher carbon corrosion current density.

In a controlled H_2/O_2 -front, start–stop test, the stop process essentially mirrors the start process as H_2 and air switch periodically at the anode inlet. As a result, the predicted accumulated carbon loss distribution down the anode channel, as shown in Fig. 15, is nearly symmetric in regions opposing the anode inlet and outlet. Figure 16 (a) shows real time CO_2 measurements at the cathode exit during the controlled start–stop test.¹⁵ It shows more carbon corrosion occurring during start than during stop, suggesting that the accumulated

Figure 14. Calculated cathode potential and carbon corrosion current distributions when H_2/O_2 front passes through 10%, 50%, and 90% of anode flow-field during a cell start from air/air state ($80\text{ }^\circ\text{C}$, $101\text{ kPa}_{\text{abs}}$, $66\% \text{ RH}_{\text{in}}$). The cell has a catalyst loading of $0.4\text{ mg}_{\text{Pt}}/\text{cm}^2$ using a 50%wt Pt/Vulcan catalyst in both anode and cathode electrodes.

Figure 15. Predicted accumulated carbon loss distribution along anode flow-field over a complete start–stop cycle for a controlled start–stop experiment as shown above the plot at 80 °C, 101 kPa_{abs}, 66% RH_{in}, and residence time of 1.5 s based on anode void volume (including flow-field and diffusion medium). The model predicts nearly symmetric carbon loss at anode inlet and outlet because the stop process essentially mirrors the start process by switching H₂ and air periodically at anode inlet.

carbon loss distribution is asymmetrical unlike what the model predicts. Figure 16(b) plots the ratio of the integrated carbon loss (equal to the ratio of the integral of the measured CO₂ concentration over time for stop over start) with respect to the residence time of the H₂/O₂ front passing through the anode flow-field. It can be seen that the stop process causes approximately 30% less carbon corrosion than the start process for the case shown in Fig. 16(a). This asymmetry becomes more significant with decreasing residence time and gradually diminishes as the residence time increases.

Figure 17 shows the measured spatially resolved mass activity map for the aged MEA from the controlled start–stop test in comparison with a new one.⁵⁵ It also indicates more carbon loss near the anode inlet, because one can easily imagine that when carbon support particles collapse, the platinum particles can come in contact with one another, which leads to coalescence of the platinum

Figure 16. (a) Real time CO₂ measurement at the exit of the cathode during H₂/air-front start-stop events with a residence time of 1.5 s based on anode void volume (including flow-field and diffusion medium). More carbon corrosion occurs during start than during stop. (b) Ratio of the integrated carbon loss (proportional to the integral of CO₂ concentration over time) for stop over start versus residence time. The ratio approaches unity as residence time increases.

Figure 17. Mass activity distribution maps for both new and aged MEAs showing impact of 200 unmitigated start-stop cycles. Test conditions: $T_{\text{cell}} = 80\text{ }^{\circ}\text{C}$, $T_{\text{dewpt}} = 85\text{ }^{\circ}\text{C}$ (anode and cathode), $P = 250/270\text{ kPa}_{\text{abs}}$ (anode/cathode), high stoichiometry flow for anode (H_2) and cathode (O_2).

particles. Additionally, as the carbon support corrodes, some of the platinum particles can become isolated from electronic conduction. In other words, more carbon loss leads to lower mass activity. The pattern of mass activity loss agrees with the CO_2 measurements discussed above, in that the outlet region (mostly damaged during start) shows a higher degree of degradation than the inlet region (mostly damaged during stop).

The asymmetry in the accumulated carbon loss (reflected by the CO_2 release rate) associated with start-stop cycling can be attributed to the difference in the state of the electrodes before a start or stop process occurs as well as the difference in the way that the electrode potentials change after a start or stop process takes place, as detailed in the following section. Asymmetry in CO_2 release rate was observed in potential cycling tests.⁵⁶ It appears that carbon corrosion occurs via a different reaction path in potential cycling compared to at a constant potential.^{56,57} However, diminishing asymmetry with increasing residence time as shown in Fig. 16 (b) implies that the effect of potential change should be secondary. The fact that the model neglects the pseudo-capacitive effect explains why it fails to predict the asymmetrical distribution in accumulated carbon loss observed in the experiments. The pseudo-capacitive effect can be rigorously accounted for by incorporating platinum

reactions that supply or consume protons in transient start-stop events. These reactions are normally neglected in a carbon corrosion model.⁵⁸ Next, we will describe a model that incorporates the pseudo-capacitance obtained from an AC-impedance measurement.

4. PSEUDO-CAPACITANCE MODEL

4.1. Mechanism Description

As shown in Fig. 14, the cathode potential changes abruptly across the H_2 /air-front. This fact warrants the inclusion of the pseudo-capacitance into the previous steady-state kinetic model.¹² It is clear that the electrode's pseudo-capacitance can supply protons in transient events and thereby reduce the cathode carbon-support corrosion rate in the case of fast moving H_2 /air-fronts. Figure 18

Figure 18. Cyclic voltammogram (CV) of a Pt electrode on an MEA. Shown are the associated electrochemical reactions at difference electrode potentials. Notice how the electrode potential changes as the cell starts from air/air conditions (diamond-tailed arrows) and stops from H_2 /air conditions (dot-tailed arrows), respectively. Experimental conditions: 25 °C, 20 mV/s, 0.4 mg_{Pt}/cm² loading.

illustrates how the electrode potential changes as the cell either starts from the air/air state or stops from the H_2 /air state; it also lists the appropriate pseudo-capacitive reactions. To better understand the effect of pseudo-capacitive charging and discharging, we will examine each of the processes in turn.

Start process (H_2 entering an air-filled anode): Originating from the air/air condition, with an approximate electrode rest potential of 1.05 V¹¹ on both anode and cathode, introduction of H_2 on the anode side creates a power source driving a load (see Fig. 1) and facile HOR forces the anode potential to near zero volts. In the portion of the anode that still has air, ORR takes place and the oxidized Pt surface is reduced according to $PtOH + H^+ + e^- \rightarrow Pt + H_2O$ plus $Pt + H^+ + e^- \rightarrow PtH$ in the potential down-transient. The protons required for these reactions are supplied from the cathode, causing the cathode potential to rise above its initial rest potential. Protons are generated at the cathode, first via further oxidation of the platinum hydroxide ($PtOH \rightarrow PtO + H^+ + e^-$), the contribution of which is determined by the pseudo-capacitance of the cathode in the potential region between ≈ 1.05 V and that where carbon corrosion sets in (ca. >1.4 V for conventional carbon-supports), and then via on-setting carbon-support oxidation and O_2 evolution when the cathode's pseudo-capacitance is expended. Thus, the cathode's pseudo-capacitance acts as a buffer against the carbon corrosion reaction during the start process. In this case, the capacitive buffer of the cathode is offset by the capacitive consumption of protons at the anode experiencing a downward potential change. If the total pseudo-capacitance of the anode between ≈ 1.05 V and that determined primarily by the ORR therein is significantly lower than the total pseudo-capacitance of the cathode, the pseudo-capacitive processes will lead to a substantial reduction in the overall H_2 /air-front start damage. An example of where this could be relevant is where low anode Pt loadings are used.

Stop process (air entering an H_2 -filled anode): Originating from the H_2 /air condition, with an anode rest potential of ≈ 0 V, introduction of air creates a load driven by a power source (see Fig. 1) and slow ORR forces the anode potential to rise significantly in the portion of the anode that air has replaced H_2 . In the potential up-transient, the PtH-terminated anode surface is oxidized according to $PtH \rightarrow Pt + H^+ + e^-$ plus $Pt + H_2O \rightarrow PtOH + H^+ + e^-$, producing protons. In the immediate vicinity of the H_2 /air-front, the

protons required for oxygen reduction can also be supplied from the anode oxidation reactions in the portion of the anode that still has H_2 , but at distances more than a few membrane-thicknesses away, they are preferentially supplied from the cathode because the in-plane transport resistance of protons makes it more favorable for them to be supplied from the cathode. Similarly to the start process, proton generation at the cathode will initially be via further oxidation of the platinum hydroxide ($PtOH \rightarrow PtO + H^+ + e^-$) and then proceed to higher potential reactions (carbon corrosion and oxygen evolution). Thus, the pseudo-capacitive reactions on *both* the anode and cathode combine to maximize the amount of protons that can be supplied in support of the O_2 reduction reaction on the anode, so that the cathode carbon-support oxidation reaction will occur to a lesser extent than in the start process, where the anode's pseudo-capacitance is subtracted from that of the cathode.

Therefore, for equal H_2 /air-front residence times, the pseudo-capacitive model would suggest lower rates of carbon-support oxidation, i.e., lower rates of CO_2 formation for the stop process if compared to the start process, which is consistent with on-line CO_2 measurements of the air exiting the cathode flow-field during H_2 /air-front start-stop events, as shown in Fig. 16.

4.2. Model Description

The pseudo-capacitive effect can be incorporated in the coupled kinetic and transport model through Eqs. (19) and (20). Here we choose to illustrate the effect through the kinetic model for simplicity. With considering the pseudo-capacitive current density, the kinetic model becomes

$$i_{\text{Power}} = [i_{\text{HOR,an}} + i_{\phi,\text{an}} = i_{\text{ORR,cath}} + i_{\phi,\text{cath}}]_{H_2\text{-rich gas/Air}} \quad (34)$$

for the power source,

$$i_{\text{Load}} = [i_{\text{ORR,an}} + i_{\phi,\text{an}} = i_{\text{COR,cath}} + i_{\text{OER,cath}} + i_{\phi,\text{cath}}]_{H_2\text{-free gas/Air}} \quad (35)$$

for the load, and again

$$i_{\text{Power}}x = i_{\text{Load}}(1 - x) \quad (13)$$

as the equal amount of current flows through both H₂/air and air/air cells. The capacitive current density appearing in Eqs. (34) and (35) is given by⁵⁹

$$i_{\phi} = -C_{\phi} \frac{dE_{\text{an or cath}}}{dt} = -C_{\phi} \frac{d(\phi_s - \phi_e)_{\text{an or cath}}}{dt} \quad (36)$$

and the charge capacity of the respective pseudo-capacitor is calculated by

$$q = \int_0^t i_{\phi} dt \leq q_{\text{max}} \quad (37)$$

Here i is the current density with the subscript representing a specific electrode reaction, capacitive current density at an electrode, or current density for the power source or the load. The surface overpotential (defined as the difference between the solid and electrolyte phase potentials) drives the electrochemical reactions and determines the capacitive current. Therefore, the three Eqs. (34), (35), and (3) can be solved for the three unknowns: the electrolyte phase potential in the H₂/air cell ($\phi_{e,\text{Power}}$), electrolyte phase potential in the air/air cell ($\phi_{e,\text{Load}}$), and cathode solid phase potential ($\phi_{s,\text{cath}}$), with anode solid phase potential ($\phi_{s,\text{an}}$) being set to be zero as a reference. The carbon corrosion current is then determined using the calculated phase potential difference across the cathode/membrane interface in the air/air cell. The model couples carbon corrosion with the oxygen evolution reaction, other normal electrode reactions (HOR and ORR), and the capacitive current in the fuel cell during start–stop.

The capacitive current is calculated based on the pseudo-capacitance value obtained in an AC-impedance measurement.⁴² Equation 37 sets the maximum stored charge, use of which can be made. In this study, $C_{\phi} = 0.2 \text{ F/cm}^2$ and $q_{\text{max}} = 0.06 \text{ C/cm}^2$ correspond to the MEA with a Pt loading of $0.4 \text{ mg}_{\text{Pt}}/\text{cm}^2$ on both anode and cathode electrodes (see Fig. 6 in the reference⁴²). Considering that the electrode's potential changes rapidly as the H₂/air-front propagates and the model caps the charge capacity, a constant value of C_{ϕ} suffices to capture accurately the pseudo-capacitive effects during start–stop.

4.3. The Pseudo-capacitive Effect

Figure 19 plots the normalized carbon loss (relative to the average value) for start and start-stop cycles in comparison with the loss of mass activity normalized to the new MEA value in one-dimensional fashion, showing good agreement. Incorporation of the pseudo-capacitance yields more carbon loss during start than during stop, as expected in Section 4.1. The ratio of stop carbon loss over start carbon loss (ca. 0.6) agrees reasonably well with the ratio of the integrated carbon loss for stop/start of approximately 0.7 from the real-time CO_2 measurement, as shown in Fig. 16(b). Clearly, it is essential to include the electrode's pseudo-capacitance in a start-stop model to understand the observed non-uniform mass activity loss from start-stop. This agreement between the model and the experiment again suggests the significance of the electrode pseudo-capacitance.

Figure 20 shows the impact of capacitive effects on the predicted amount of local carbon corrosion as a function of the

Figure 19. Predicted carbon loss distribution along anode flow-field channel over a complete H_2 /air-front start-stop cycle using the pseudo-capacitance model in comparison with one-dimensional, normalized mass activity from Fig. 17. The pseudo-capacitance value used in the model is obtained from AC-impedance measurements as described in references (42, 43).

Figure 20. The impact of a faster H_2 /air-front moving through the anode flow-field. 100% relative carbon loss is defined as the localized damage prediction when no pseudo-capacitance is considered in the model. Significantly less carbon corrosion is expected at the anode inlet region as the speed of H_2 /air-front increases but much less benefit at the anode outlet region.

H_2 /air-front residence time. 100% here refers to the extent of local carbon-support corrosion predicted without considering pseudo-capacitive effects. Apparently, pseudo-capacitive effects are expected to play a minor role, if the H_2 /air-front residence time is long due to the limited capacitance. Therefore, at long residence times, the difference made by considering the pseudo-capacitive effect is quite small. This explains why simple steady-state kinetic models without including pseudo-capacitive effects work well when predicting carbon-support corrosion in accelerated H_2 /air-front experiments which use long residence times to accelerate the damage.¹² On the other hand, at short H_2 /air-front residence times, characteristic of what one would observe in a well-designed PEMFC system, the pseudo-capacitive effect becomes rather significant. Therefore, inclusion of pseudo-capacitive effects is critical when modeling real-world applications.

Since the time scales for establishing local H_2 starvation events are on the order of seconds or 10's of seconds,^{11,14} pseudo-capacitive effects will not be important.

5. SUMMARY AND OUTLOOK

The carbon-support corrosion models developed here are based on measured electrode kinetics and the concept that, in a situation when a fuel cell has air on the cathode and a combination of H_2 and air regions on the anode, the former act as a power source (H_2/O_2 fuel cell) that drives corrosion in the latter (air/air-corrosion cell). The kinetic model has yielded much insight into the origin and impact of carbon-support corrosion. It can serve as an efficient tool to guide new material development and MEA design. For example, since corrosion can effectively be mitigated if the OER kinetics are fast enough to compete with COR, electrode materials that favor the OER reaction can serve to make electrodes much more resistant to corrosion. Additionally, given that the rate of COR is limited by oxygen crossover in the instance of localized anode H_2 starvation, incorporation of membrane materials that minimize oxygen permeation will serve as an effective mitigation strategy.

The coupled kinetic and transport model is needed to predict when local H_2 starvation occurs and how it affects the carbon corrosion rate. The ability to predict length scales of H_2 depletion is helpful in designing advanced flow-fields that prevent liquid water from accumulating to form an H_2 -starved region of sufficient size for corrosion to be possible. Similarly, predicting time scales for these starved regions to develop is valuable for developing system mitigation strategies that help to remove accumulated liquid water and N_2 before a local H_2 -starved region becomes fully developed. The coupled kinetic and transport model is also necessary for simulating an extended stop process in which the location and longevity of an H_2/O_2 front are determined by coupled kinetic and transport processes.

The pseudo-capacitance model is essential in predicting the observed asymmetrical carbon loss distribution along the flow channel that develops after a number of start–stop cycles. The pseudo-capacitive effect must be taken into account in simulating start–stop processes (i.e., transient H_2 /air-front events). It provides useful information on the strategy of using a fast purge to mitigate cathode carbon-support corrosion, that is, how fast the H_2/O_2 front needs to be to make full use of the stored charge capacity. Because it takes longer for local H_2 starvation to fully develop, the

capacitive effect is expected to be less significant in the case of local H_2 starvation.

Recent kinetic studies indicate that carbon corrosion can be significant under normal transient operation.^{56,57,60–62} The rate of voltage change, common in the automotive application, enhances cathode carbon-support corrosion.¹⁶ Hence, further model improvement shall be focused on finding the carbon corrosion kinetics associated with voltage cycling. Currently, the relationship between fuel cell performance decay and accumulated carbon-support loss is only empirical.²² More effort has to be made to incorporate mechanisms that can accurately quantify voltage decay with carbon-support loss.^{31,32}

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LIST OF SYMBOLS

a	electrochemically active surface area of an ingredient in an electrode, cm^2/mg
C_ϕ	electrode pseudo-capacitance, $F/cm^2_{\text{electrode}}$
c_i	molar concentration of species i , mol/cm^3
D_i	effective diffusion coefficient of species i , cm^2/s
$D_{i,mix}$	molecular diffusion coefficient of species i in a multi-component mixture, cm^2/s
$D_{K,i}$	Knudsen diffusion coefficient of species i , cm^2/s
d	pore diameter of an electrode, cm
E^o	standard equilibrium (or reversible) potential of an electrode reaction, V
$E^{\text{dry or wet}}$	activation energy for gas transport in the dry (or wet) phase of membrane, J/mol
E^{rev}	activation energy of an electrode reaction at zero overpotential, J/mol
$E_{\text{an or cath}}$	electric potential of anode (or cathode) electrode, V
F	Faraday constant, $C/equiv$
i	current density, A/cm^2

i_o	exchange current density of an electrode reaction, $A/cm^2_{Pt \text{ or } C}$
i_{x,O_2}	O_2 crossover current density, A/cm^2
K^s	permeability of a porous medium, cm^2/s
K^m	permeability of gaseous species through membrane, $mol \text{ cm}/(cm^2 \text{ s kPa})$
L	loading of an ingredient in an electrode, mg/cm^2
M	molecular weight of a species, g/mol
m	index for carbon weight loss dependence in the COR kinetics equation
n	number of electrons transferred in an electrode reaction
p	pressure, partial pressure of a species, kPa
q_{max}	maximum stored charge, $C/cm^2_{electrode}$
R	universal gas constant, $J/mol/K$
R_{H^+}	proton transport resistance, $\Omega \text{ cm}^2$
$r_{Pt/C}$	weight ratio of ingredient Pt to carbon support in an electrode
RH	relative humidity, %
s	stoichiometry of a species in an electrode reaction
T	temperature, $^{\circ}C$ or K
t	time, s
v	gas velocity, cm/s
x	normalized location of H_2/O_2 front at the anode
x_i	mole fraction of species i in a gas mixture

Greek Symbols

α_a	anodic transfer coefficient of an electrode reaction
α_c	cathodic transfer coefficient of an electrode reaction
δ	thickness, cm
ε	porosity
ϕ	electric potential, V
γ	reaction order of a species in an electrode reaction
η	charge transfer overpotential of an electrode reaction, V
κ	proton conductivity, S/cm
σ	electron conductivity, S/cm
τ	tortuosity

μ_{mix}	viscosity of a gas mixture, Pa s
θ	Mass fraction of carbon support that has been lost

Subscripts

an	anode
cath	cathode
CL	catalyst layer
e	electrolyte conducting protons
mem	membrane
s	solid conducting electrons

Superscripts

ref	reference
sat	saturated

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