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Water transport during startup and shutdown of polymer electrolyte fuel cell stacks

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ABSTRACT

A dynamic three-phase transport model is developed to analyze water uptake and transport in the membrane and catalyst layers of polymer electrolyte fuel cells during startup from subfreezing temperatures and subsequent shutdown. The initial membrane water content (λ, the number of water molecules per sulfonic acid site) is found to be an important parameter that determines whether a successful unassisted self-start is possible. For a given initial subfreezing temperature at startup, there is a critical λ (λ_h), above which self-start is not possible because the product water completely engulfs the catalyst layers with ice before the stack can warm-up to 0 °C. There is a second value of λ (λ_l), below which the stack can be self-started without forming ice. Between λ_l and λ_h, the stack can be self-started, but with intermediate formation of ice that melts as the stack warms up to 0 °C. Both λ_l and λ_h are functions of the initial stack temperature, cell voltage at startup, membrane thickness, catalyst loading, and stack heat capacity. If the stack is purged during the previous shutdown by flowing air in the cathode passages, then depending on the initial amount of water in the membrane and gas diffusion layers and the initial stack temperature, it may not be possible to dry the membrane to the critical λ for a subsequent successful startup. There is an optimum λ for robust and rapid startup and shutdown. Startup and shutdown time and energy may be unacceptable if the λ is much less than the optimum. Conversely, a robust startup from subfreezing temperatures cannot be assured if the λ is much higher than this optimum.

1. Introduction

Polymer electrolyte fuel cells (PEFC) for transportation must be able to start unassisted from temperatures below −20 °C and produce 50% of their rated power within 30 s while using less than 5 MJ of fuel energy for startup and shutdown of an 80-kWe system [1]. At subfreezing temperatures, the water produced by the electrochemical reaction coats the cathode catalyst with ice that reduces the effective electrochemically active surface area (ECSA) and may terminate the reaction. It may be possible to prevent ice formation by operating at low current densities and using dry gas feeds at high flow rates, but these operating conditions lead to unacceptable startup times and energies. Fast start may involve the formation of ice and presents the challenge to effectively manage the buildup of ice [2]. A proper understanding of water transport during startup (and the previous shutdown) is essential to determining the conditions under which the stack can be started rapidly from subfreezing temperatures, even if some ice may be formed initially at startup.

Isothermal behavior of single cells at subfreezing temperatures has been reported in a number of investigations. Hishinuma et al. [3] monitored voltage decay at constant current of a 104-cm^2 cell placed inside a climate-controlled chamber at −10 to −25 °C. They concluded that a cell could not be started from temperatures below −5 °C without external heating. Oszipok et al. [4] extended this study to include the effect of initial membrane water content on isothermal potentiostatic behavior of a single cell. They inferred from their experimental data that initial membrane drying is beneficial in successful self-start from −20 °C, but that the membrane should not be too dry. Tajiri et al. [5] confirmed the beneficial effect of initial membrane drying and also investigated the effects of initial gas purge and membrane thickness on cold-start behavior. In follow-up papers, Ge and Wang [6,7] reported observations from visualizations of ice formation and cyclic voltammetry data on the effect of ice coverage on the oxygen reduction kinetics. Pinton et al. [8] conducted isothermal and galvanostatic tests to study cold-start behavior as a function of various operating parameters, including initial water content, cell voltage and current density. They observed an optimal wetting level that maximizes the heat generated from the electrochemical reaction.

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Nomenclature

A	specific area
a	activity
D	diffusivity
F	Faraday constant
h	mass transfer coefficient
I	current density
$\dot{I}$	volumetric reaction rate
J	Leverett function
K	absolute permeability
k_r	relative permeability
S	water saturation level
t	time
u	velocity
y	transverse direction
β	osmotic drag coefficient
δ	step function
ε	volume fraction
κ	ionic conductivity
λ	membrane water content
μ	viscosity
ρ	molar density
ρ_m	membrane density divided by equivalent weight
σ	surface tension

Subscripts/superscripts

eff	effective
H^+	proton
h	upper limit
i	ice, initial
l	liquid water, lower limit
m	membrane, ionomer
max	maximum
ORR	oxygen reduction reaction
s	saturation
v	vapor

There are only limited experimental and theoretical studies on non-isothermal startup from subfreezing temperatures. Ahluwalia and Wang [2] investigated the conditions for rapid start including the effect of cell voltage and heat capacity of stack materials. Conti [9] reports experimental data on time and energy consumed in cold-start of a short stack. Other manufacturers [10–12] have also reported successful startup from temperatures down to −30 °C. Multi-dimensional models of cold-start have also started to appear in the open literature [13,14].

Water removal from fuel cells by gas purging during shutdown is a subject of current interest. Sinha and Wang [15] formulated a simple model to characterize water transport across the membrane and gas diffusion layers in purge drying. Tajiri et al. [16] presented some initial data on the drying process using high-frequency resistance of the cell as an indicator of the water content. Owejan et al. [17] examined water transport in fuel cells by using in situ and ex situ methods and used the data to formulate a one-dimensional model for calculating the effectiveness of cathode purge for removing water from fuel cells at shutdown.

Many publications have recently appeared on the fundamental properties of membranes and electrocatalytic activity at subfreezing temperatures. Thompson et al. [18] have investigated low temperature proton transport in Nafion using direct current four-point probe for conductivity measurements and differential scanning calorimetry for melting and freezing of membrane water. In subsequent work, Thompson et al. [19–21] developed an experimental procedure to measure oxygen reduction reaction kinetics at subfreezing temperatures and investigated ice formation, water (charge) storage, current distribution, and voltage losses during isothermal cold-start. Gallagher et al. [22] measured electro-osmosis and water uptake in polymer electrolytes in equilibrium with water vapor at low temperatures. References [2,18–22] may be consulted for other literature on membrane properties and electrocatalyst activities at low temperatures.

Table 1
Stack parameters.

Stack gross power	93.5 kW
Stack weight	56 kg
Number of cells	452
Cell voltage at rated power	663 mV
Platinum loading (*a*/*c*)	0.1/0.2 mg cm^{-2}
Active area per cell	329 cm^2
Active area to total area	85%
Graphite bipolar plate thickness	200 μm
Gas channel depth/width	0.5/3 mm
Land shoulder width	0.6 mm
GDL thickness	260 μm
GDL porosity, ε	60%
GDL gas permeability, K	2.55×10^{-13} m^2
GDL contact angle	100°
Catalyst layer thickness (*a*/*c*)	4/6 μm
Catalyst layer porosity, ε	46%
Ionomer volume fraction, ε_m	23%
Membrane thickness	25 μm
Bulk density of ice	500 kg m^{-3}

In this work, we investigate the effect of water transport on startup and shutdown at subfreezing temperatures. It builds on the earlier work reported in Ref. [2] and provides a theoretical underpinning for the experimental observations concerning the effect of initial water content on startup from cold [4,5,8]. It also reports theoretical purge drying of stacks to prepare membrane electrode assemblies for subsequent successful startup from cold temperatures.

2. Water transport model

We have formulated a model to determine water transport during startup and shutdown. The model tracks water transport across the membrane and the ionomer in the catalyst layers in terms of λ, the number of water molecules per sulfonic acid site, by solving a set of transient equations that consider diffusion and electro-osmotic drag. Eq. (1) describes water transport across the solid membrane.

$$\frac{\partial}{\partial t}(\rho_m \lambda) = \frac{\partial}{\partial y}\left(\rho_m D_\lambda^{eff}\frac{\partial \lambda}{\partial y} - \beta_\lambda \frac{I_{H^+}}{F}\right) \quad (1)$$

During startup from subfreezing temperatures, water can be present in the catalyst layers in three phases: solid ionomer, interstitial vapor and ice. The following conservation equations describe the movement of water within the ionomer (subscript *m*), vapor (subscript *v*) and ice (subscript *i*) phases by various mechanisms, including interfacial mass transfer.

$$\frac{\partial}{\partial t}(\rho_m \varepsilon_m \lambda) = \frac{\partial}{\partial y}\left(\rho_m \varepsilon_m D_\lambda^{eff}\frac{\partial \lambda}{\partial y} - \beta_\lambda \frac{I_{H^+}}{F}\right) + \frac{\dot{I}_{ORR}}{2F} - h_m A_m(\rho_{mv} - \rho_v) \quad (2)$$

$$\frac{\partial}{\partial t}(\varepsilon \rho_v) = \frac{\partial}{\partial y}\left(D_v^{eff}\frac{\partial \rho_v}{\partial y}\right) + h_m A_m(\rho_{mv} - \rho_v) - h_c A_c(\rho_v - \rho_s) \quad (3)$$