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Catalytic hydrogen–oxygen reaction in anode and cathode for cold start of proton exchange membrane fuel cell

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ABSTRACT

Fuel cell vehicles (FCVs) have shown the potential of commercialization in recent years. The concerns on the startup ability of proton exchange membrane (PEM) fuel cell stack from subfreezing temperature have risen. The hydrogen–oxygen catalytic reactions assisted cold start method is developed and analyzed in this study. It utilizes a small amount of hydrogen/air mixture to react at low temperature in the catalyst layers (CLs) through platinum catalyst. The interactions between this assisted method and various startup modes are the major issue to be discussed. Anode catalytic reaction with air mole fraction higher than 16% is effective to assist a 30-cell stack starting from -25°C within 13 s in maximum power mode. However, cathode catalytic reaction cannot sustain a successful startup. The anode humidification effect plays an important role to reduce the stack resistance, and to increase the inherent heat generation rate. In maximum power mode and high current density constant power mode, anode catalytic reaction assisted cold start can be achieved within 10–20 s from -40°C . Anode air mole fraction must be higher than 18% to ensure the successful cold start in these two modes. For constant power mode, the operating power must be lower than 12 W per cell. In constant current mode, when the current density is low, there would be less demand for anode catalytic reaction to achieve successful startup from -40°C , indicating that lower current density operations have better survivability in low temperature. Nevertheless, much longer start duration is required for lower operating current. Generally, high current density operating mode with high air mole fraction is a more practical and energy efficient cold start strategy, as the startup time can be reduced significantly. Cold start from about -20°C without ice accumulation is feasible using this method, which may have reduced concern about degradation. Increasing the volume of CL (porosity and thickness) also helps reduce the ice formation.

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Nomenclature	
<i>a</i>	water activity
<i>A</i>	cell geometric area, m ²
ASR	area specific resistance, Ω·cm ²
<i>c</i>	mole concentration, mol m ⁻³
<i>C_p</i>	specific heat, J kg ⁻¹ K ⁻¹
<i>D</i>	mass diffusivity, m ² s ⁻¹
<i>E</i>	activation energy, kJ mol ⁻¹
EW	equivalent weight of membrane, 1.1 kg mol ⁻¹
<i>F</i>	Faraday's constant, 96487 C mol ⁻¹
<i>h</i>	convective heat transfer coefficient, W m ⁻² K ⁻¹ ; enthalpy, J mol ⁻¹
<i>I</i>	current density, A cm ⁻²
<i>j</i>	exchange current density, A cm ⁻²
<i>k</i>	thermal conductivity, W m ⁻¹ K ⁻¹ ; pre-exponential factor
<i>K</i>	permeability, m ²
<i>M</i>	molecular weight, kg mol ⁻¹
MEA	membrane electrode assembly
<i>p</i>	pressure, Pa
<i>P</i>	power, W
<i>Q̇</i>	heat transfer rate, W
<i>R</i>	universal gas constant, J mol ⁻¹ K ⁻¹ ; reaction rate, mol m ⁻³ s ⁻¹
RH	relative humidity
<i>s</i>	volume fraction
<i>S</i>	source terms
<i>t</i>	time, s
<i>T</i>	temperature, K
<i>T⁰</i>	standard temperature, 298 K
<i>V</i>	voltage, V
<i>Greek letters</i>	
<i>α</i>	transfer coefficient
<i>δ</i>	thickness, m
<i>ε</i>	porosity
<i>ζ</i>	water transfer rate, s ⁻¹
<i>γ</i>	phase change rate, s ⁻¹
<i>η</i>	overpotential, V
<i>κ</i>	electric conductivity, S m ⁻¹
<i>λ</i>	water content in ionomer
<i>μ</i>	dynamic viscosity, kg m ⁻¹ s ⁻¹
<i>ξ</i>	stoichiometry ratio
<i>ρ</i>	density, kg m ⁻³
<i>ω</i>	volume fraction of ionomer in catalyst layer
<i>Subscripts and superscripts</i>	
<i>a</i>	anode
<i>act</i>	activation
<i>anode_cata</i>	anode catalytic reaction
<i>atm</i>	atmosphere
BP	bipolar plate
<i>c</i>	cathode, capillary
<i>cata</i>	catalytic reaction
<i>cathode_cata</i>	cathode catalytic reaction
Cell	cell characteristic
<i>channel</i>	flow channel
CL	catalyst layer
<i>conc</i>	concentration
<i>ec</i>	electrochemistry reaction
<i>eff</i>	effective
<i>env</i>	environment
<i>eq</i>	equilibrium
<i>f</i>	frozen
<i>fl</i>	fluid phase
<i>fmw</i>	frozen membrane water
<i>g</i>	gas
GDL	gas diffusion layer
H ₂ O	water
<i>i</i>	the <i>i</i> th components
<i>ice</i>	ice
<i>lq</i>	liquid water
<i>mem</i>	membrane
<i>N</i>	cell number
<i>nernst</i>	Nernst
<i>nf</i>	non-frozen
<i>nmw</i>	non-frozen membrane water
<i>ohmic</i>	ohmic
<i>out</i>	outlet, output
<i>P</i>	power
<i>sat</i>	saturation
<i>sl</i>	solid phase
<i>Stack</i>	stack characteristic
<i>sup_lq</i>	supercooled water
<i>T</i>	energy (for source term)
<i>vp</i>	water vapor
<i>wall</i>	surrounding wall of the stack
<i>l-i</i>	liquid to ice
<i>n-f</i>	non-frozen membrane water to frozen membrane water
<i>n-i</i>	non-frozen membrane water to ice
<i>n-l</i>	non-frozen membrane water to liquid

Introduction

Proton exchange membrane (PEM) fuel cell has made significant progress from fundamental research to practical applications such as automotive, stationary and portable power systems in recent years, especially for transportations [1]. The US department of energy (DOE) has reported that the current status of

PEM fuel cell system cost is reduced to \$55/kW, the durability with <10% voltage degradation is over 5000 h in laboratory testing, and the system efficiency at full power has reached 53% [1]. Importantly, cold start has become one of the critical issues for the commercialization of PEM fuel cells. Strict cold start targets have been set recently. DOE set the latest target of achieving cold start from -40 °C, and it requires that 50% power

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