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Evaluating the impact of enhanced anode CO tolerance on performance of proton-exchange-membrane fuel cell systems fueled by liquid hydrocarbons

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ABSTRACT

Recent advances in anode electrocatalysts for low-temperature PEM fuel cells are increasing tolerance for CO in the H_2-rich anode stream. This study explores the impact of potential improvements in CO-tolerant electrocatalysts on the system efficiency of low-temperature Nafion-based PEM fuel cell systems operating in conjunction with a hydrocarbon autothermal reformer and a preferential CO oxidation (PROx) reactor for CO clean-up. The incomplete H_2 clean-up by PROx reactors with partial CO removal can present conditions where CO-tolerant anode electrocatalysts significantly improve overall system efficiency. Empirical fuel cell performance models were based upon voltage–current characteristics from single-cell MEA tests at varying CO concentrations with new Pt–Mo alloy reformate-tolerant electrocatalysts tested in conjunction with this study. A system-level model for a liquid-fueled PEM fuel cell system with a 5 kW full power output is used to study the trade-offs between the improved performance with decreased CO concentration and the increased penalties from the air supply to the PROx reactor and associated reduction in H_2 partial pressures to the anode. As CO tolerance is increased over current state-of-the-art Pt alloy catalysts, system efficiencies improve due primarily to higher fuel cell voltages and to a lesser extent to reductions in parasitic loads. Furthermore, increasing CO tolerance of anode electrocatalysts allows for the potential for reduced system costs with minimal efficiency penalty by reducing PROx reactor size through reduced CO conversion requirements.

1. Introduction

Expanding the market for proton-exchange-membrane (PEM) fuel cell systems, specifically for portable/mobile applications involving liquid hydrocarbon fuels, requires integration of a fuel reformer and associated balance of plant with the fuel cell stack. For low-temperature Nafion-based PEM fuel cells, integration with hydrocarbon fuel processing requires near-complete removal of CO from the reformate stream when the stack employs conventional Pt-based anode electrocatalysts. The need for hydration of the Nafion membrane requires operating temperatures below 90 °C at typical PEM fuel cell pressures. At such temperatures, pure Pt electrocatalysts as well as commercial PtRu anode electrocatalysts cannot effectively oxidize CO at concentrations above 100 ppm in the anode without unacceptable losses in current density at typical PEMFC operating voltages (0.6–0.8 V).

Current CO clean-up strategies for linking conventional low-temperature PEM fuel cell stacks with hydrocarbon reformers greatly increase the overall system size and complexity because of high temperatures in the fuel processor and the need for heat exchangers and reactors to cool the reformate, clean-up and burn the CO in the reformate, and capture the necessary water for running the reformer, either as a full endothermic steam reformer or an autothermal reformer. Such a system with an autothermal reformer is illustrated in the process schematic in Fig. 1, which shows a system that relies on a preferential CO oxidation (PROx) reactor for clean-up of the reformate. Besides the PROx reactor [1,2], other approaches considered for reformate CO removal include pressure-swing absorption (PSA) reactors [3] and Pd-based membrane purifiers [4,5]. The latter two approaches provide near-complete CO elimination, whereas the PROx reactor only provides partial clean-up. However, the PROx system avoids the penalties of including two large reactors and the regeneration process associated with PSA or the increased parasitic loads associated with high-pressure reformer operation required by Pd-based membranes. Furthermore, a PROx system has flexibility in that as anode electrocatalysts are developed with improved CO tolerance, the requirements on the PROx reactor – in terms of CO conversion and CO selectivity – may be reduced. This study utilizes a system model to explore how improved anode electrocatalysts with

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Nomenclature

A_{cell}	geometric area of single electrochemical cell in fuel cell stack (cm^2)
F	Faraday's constant = 96,485 (C gmol electrons^{-1})
$h_{H_2,comb}$	lower enthalpy of combustion of H_2 (J kg^{-1})
$h_{HC,comb}$	lower enthalpy of combustion of hydrocarbon (J kg^{-1})
i	average effective current density per unit area in the fuel cell stack (A cm^{-2})
$\dot{m}_{H_2,anode,in}$	mass flow rate of H_2 into the anode (kg s^{-1})
$\dot{m}_{HC,in}$	mass flow rate of hydrocarbon into fuel reformer (kg s^{-1})
n_{cells}	number of electrochemical cells in fuel cell stack
O/C	oxygen (from O_2) to carbon (from fuel) atomic ratio in fuel reformer inlet
S/C	steam to carbon (from fuel) ratio in fuel reformer inlet
T_{amb}	ambient temperature (°C or K)
$T_{WGS,out}$	water-gas-shift outlet temperature (K)
V_{cell}	voltage across an individual electrochemical cell in stack (V)
$\bar{W}_{H_2}$	molecular weight of H_2 (g gmol^{-1})
$\dot{W}_{lost}$	parasitic power lost due to balance of plant components and DC–AC inverter (W)
$\dot{W}_{net}$	net electrical power out (W)
ε_{H_2}	fraction of anode inlet H_2 utilized in stack
η_{BOP}	effective efficiency associated with power delivered to power produced by stack
η_{FC}	effective efficiency of fuel cell stack
η_{FP}	effective efficiency of fuel processor and Pd alloy membrane purifier combined
η_{th}	overall effective system efficiency
ξ_{CO}	anode CO-tolerance factor as defined in Section 2

increased CO tolerance can impact the overall system performance of a hydrocarbon-fueled PEM fuel cell system utilizing a PROx reactor for CO clean-up.

Recent advances in nanoparticle catalyst synthesis have shown that controlled alloy and nano-structured electrocatalysts may allow PEM fuel cells to operate at relatively high current (and thus power) densities on H_2 streams with CO levels of a few hundred ppm or more, even at the low temperatures required for Nafion-based PEM fuel cells [6,7]. This study builds on recent testing of PEM fuel cell membrane electrode assemblies (MEAs), which show CO tolerance of PtMo and PtRu alloy anode electrocatalysts, with relatively stable operation at 100 ppm CO or more [8–10]. The advances in anode electrocatalyst design suggest that with a new generation of CO-tolerant electrocatalysts, the reduced losses in current density due to CO at typical operating voltages may allow for reduced reformate clean-up and simplify a PEM fuel cell system with hydrocarbon fuel processing for H_2 production. In general, the increased tolerance for CO in PEM fuel cell anodes reduces the need for H_2 purification and thereby the penalties in overall efficiency resulting from fuel processing/purification in hydrocarbon-fueled PEM fuel cell systems. There is value in studying the system impacts of improved CO tolerance in Nafion-based PEM fuel cells.

Modeling the hydrocarbon fuel processing, PROx reactor CO clean-up, PEM fuel cell stack, and the balance of plant presents significant challenges because of the complex significant thermal integration and mass flow recycling for recovering water in the system. Balance of plant components including air compressors/blowers, liquid pumps, and a radiator fan present parasitic loads to the system that will vary strongly with operating conditions, power loads, and individual component performance. For the high level analysis, integrated system models with lumped analysis for individual components [5,11–15] provide an effective means for evaluating system design and performance of complex integrated PEM fuel cell power plants with hydrocarbon fuel processors. These studies have been conducted with various fuel reforming and CO-removal systems. However to date, no system models have clearly examined the impact on system performance of increased CO-tolerance in PEM fuel cell stacks and associated reduction in purification requirements. Past studies with PROx reactors in the system have often assumed that the PROx is 100% effective or that the CO is reduced to sufficiently low concentrations entering the fuel cell stack that performance is unaffected [13].

The current study builds on previous work [15] which explored the implications of complete H_2 purification using Pd-based membranes in PEM fuel cell systems running on liquid hydrocarbon fuels. The system-level model, which performs iterative mass, species, and energy balances on the fuel processor, fuel cell stack, and balance of plant components, has been modified for this study to explore the effects of partial H_2 clean-up using preferential oxidation reactors (PROx) for partial CO removal. The model results explore how increasing CO tolerance of anode electrocatalysts reduces the parasitic penalties in terms of air supply and unwanted H_2 consumption for the PROx reactor and thereby improves the system performance. Empirical fuel cell performance models to predict the effects of CO concentrations on the fuel cell performance were based upon voltage–current characteristic from single-cell MEA tests at varying CO concentrations with new alloy reformate-tolerant electrocatalysts being developed at the University of Maryland [6]. This study provides a clear indication of how future advances in CO-tolerant anode electrocatalysts can impact system efficiencies and preferred operating conditions for hydrocarbon-fueled PEM fuel cell systems.

2. System model description

The system flow diagram and component integration for a hydrocarbon-fueled PEM fuel cell generator is illustrated in the schematic of Fig. 1. This paper focuses on this particular configuration, which integrates a PEM fuel cell stack with a liquid-fueled autothermal reformer (ATR) with a subsequent water-gas-shift (WGS) reactor and a PROx reactor with proper thermal management for H_2 purification. Additional balance of plant subsystems, which account for parasitic loads, are also illustrated in Fig. 1 with the dominant parasitic loads coming from the air compressors for the fuel processor, cathode air, and PROx reactor and from the radiator fan. Electric motors and inverters for power conversion are not shown in Fig. 1, but both are incorporated into the model with constant efficiencies of 90 and 93%, respectively.

Components for the cathode-side air supply, exhaust burning, cooling, and water recovery are similar to those presented in an earlier study with a similar modeling approach [15]. The key difference between the current and previously reported systems is the replacement of the Pd membrane purifier in the previous study with a PROx reactor and associated air compressor and heat exchanger to cool the PROx effluent before it enters the fuel cell. Furthermore, Pd membrane purification was integrated with the water-gas-shift reactor in the previous study, while the present system incorporates just the water-gas-shift reactor without a membrane, as shown in Fig. 1.

The fuel processor is an autothermal fuel reformer (ATR) operating on a model kerosene (or JP-8), represented as $C_{12}H_{23}$ [15]. The autothermal reformer is maintained at constant steam to carbon (S/C = 1.6) and oxygen to carbon (O/C = 0.8) ratios. This condition is