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# Original article

# Automation and control of an experimental protonic membrane steam methane reforming system

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# ABSTRACT

Nickel dispersion on doped barium-zirconate ceramics is a state-of-the-art material formulation used to fabricate proton conducting membranes that can reform methane at lower operational temperatures (600 to 800 °C). Although steady-state operational data have been reported for these ion-conducting ceramic reformers, transient datasets are uncommon and not readily available. Moreover, the automation of protonic membrane reformers is a major technical challenge for the commercialization of modular thermo-electrochemical hydrogen generators with highly nonlinear process dynamics. Here, a multi-input multi-output feedback control scheme has been designed from a relative gain array analysis of three process variables for an experimental 500 W (thermal and electrochemical power consumption) protonic membrane reforming system. Specifically, the proposed control architecture automatically calculates hydrogen separation rate setpoints while safely and effectively reaching hydrogen production rate setpoints and desired steam-to-carbon ratios. The control architecture also drives the system to 99.6% methane conversion at a current density of  $0.564 \pm 0.0125$  A·cm<sup>-2</sup> at 788 °C. Internal temperature fluctuations are mostly constrained to  $\pm$  6.00 °C  $\cdot$ min<sup>-1</sup>, which improves catalyst longevity when operating at hydrogen recovery rates exceeding 50%. Chief among these findings is an experimental demonstration of a control scenario that alters the hydrogen production rate setpoint every 150 min without sacrificing system-wide controllability. Integrator windup scenarios and counterproductive control actions are also avoided through rational controller design and proper controller tuning exercises. Industrial-scale applications of protonic membrane reformers may therefore be automated to control up to three process variables and have up to three additional control degrees of freedom for process intensification and optimization, making for well-governed, autonomous hydrogen generation units.

## 1. Introduction

The evolution of the industrial chemical engineering discipline is primarily driven by the need to meet societal demands at scale and is constrained by economic optimization or technological advancements. Fortunately, the academic counterpart to industrial chemical engineering maintains an affinity for hybridizing applied sciences with the fundamental chemical engineering principles – transport phenomena, reaction engineering, thermodynamics, and process systems and control (Scriven, 1991) – enabling the seeding of novel ideas that could eventually offer viable solutions to current and future chemical manufacturing challenges. This is precisely why mature steam methane reforming (SMR) technologies are being put under renewed and scholarly lines of inquiry to enable hydrogen generation and purification at smaller commercial scales that would otherwise be cost-prohibitive with the reforming technologies of today.

Nevertheless, existing SMR technologies that catalytically reform hydrocarbons have a rich industrial history and are, after eighty-six years of academic and operational research, highly optimized processes. The first tubular and nickel-catalyzed methane reformers had operating domains of 1 to 4 bar and could maintain material integrity at 800 °C outlet temperatures (Murkin and Brightling, 2016). These early reformers also had significant pressure drops due to packedbed orientations and less-than-optimal catalyst particle geometries. As advances in tube metallurgy came to be, both the tubular reformer operating temperatures and pressures dramatically increased to modern industrial operating conditions at 20 to 30 bar and 900 °C (Rostrup-Nielsen and Hansen, 2011). Efforts to limit carbon formation reactions

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in SMR units at these new operational conditions led to the rapid chemical synthesis of anti-coking catalysts, and the reforming industry was presented with advanced catalyst geometries and compositions to enhance methane conversion in harsh or corrosive environments.

Reformer geometries and convection zones have also evolved with hydrogen-production scales, though 10<sup>3</sup> and 10<sup>4</sup> N m<sup>3</sup> h<sup>-1</sup> production plant capacities typically require furnaces fueled by natural gas combustion (Häussinger et al., 2011) to supply energy to the process regardless of scale. Traditionally, a functional reformer design enables the unit operation to generate maximum temperatures at the outlet regions of reformer tubes to maximize hydrocarbon conversion. In standard reforming plant designs, the reformer is fed pre-reformed methane from natural gas, and water gas shift (WGS) reactors are positioned in series for the further conversion of carbon monoxide to hydrogen. A pressure swing adsorption unit often follows this sequence of reactors to purify the hydrogen target product. Emerging plant designs include electrically-heated reformer units and fuel-cell-type membranes with integrated hydrogen separation. Electrically-heated reforming technologies improve heat flux and heat distribution, whereas membrane reformers permanently shift chemical equilibria towards enhanced hydrogen production rates through the removal of hydrogen from reaction zones (Häussinger et al., 2011).

In Citmaci et al. (2024), our laboratory designed and constructed an experimental 100 W electrified steam methane reforming system with a nickel-zirconia catalyst washcoat to produce  $1.55 \times 10^{-2}$  kg H<sub>2</sub> day<sup>-1</sup>. The catalytic washcoat, of this and other electrically-heated reformers (Wismann et al., 2019), enables near-complete hydrocarbon conversion and robust stability while operating in the 800 to 900 °C temperature range at 1.00 bar. We have also shown that to automate the temperature ramps of the electrified reformer, proportional-integral (PI) feedback control can be employed. In addition, model predictive control, with constraints on electric current deviations, was implemented to demonstrate optimal control over the hydrogen production rate of the same electrified reformer. Ultimately, an improved operational longevity of the FeCrAl reformer tube and nickel-zirconia catalyst was observed when operating this system under the model predictive control architecture, which also lowered electrical power consumption by 5.66 W (or 6.13%) compared to the operation of the system under proportional-integral (PI) feedback control.

Unlike electrified SMR systems, the use of ion-conducting ceramics to fabricate membrane reformers is an advanced engineering approach that amalgamates fundamental unit operations to generate and purify hydrogen. Thermal catalysis, gas separation through electrochemical catalysis, gas compression, and Joule-heating, all occur simultaneously in ceramic membrane reformers on a 400 µm scale. The important work of Fjeld et al. (2017) explored the use of a barium zirconate-based protonic membrane reformer with nickel dispersion on electrodes as the thermo-electrochemical catalyst. Specifically, a  $BaZr_{0.8-x-y}Ce_{x}Y_{y}O_{3-\delta}$ (BZCY) electrolyte was synthesized to suppress the carbon dioxidebased decomposition of previously tested fuel-cell cerates, providing long term material stability in the presence of steam methane reforming by-products. The same study estimated a total equipment purchase cost of \$ 30,573 (in 2025 \$US, adjusted for inflation) per 25 kg H<sub>2</sub> day<sup>-1</sup> hydrogen generator. The projected reduced capital and operating cost of these compact PMR generators depends on system automation and complete thermal integration (Field et al., 2017). Decentralized PMR generators will not have traditional operational personnel and thus require advanced automation architectures, and complete thermal integration will allow these smaller production-scale thermo-electrochemical technologies to offer the same efficiencies of large hydrogen production plants.

In the chemical engineering literature, only a small subset of feedback control works involving proton exchange membranes (PEM) or protonic membrane reactor units exist. Most of these works are simulation-based; therefore, important disturbance phenomena and measurement uncertainties from the real process are not accurately accounted for in tests of controller stability and performance. Notwithstanding, we consider works on PEM fuel cells to be of importance to this work, since the control objectives of different hydrogen energy systems often overlap. In particular, Lin et al. (2006) explored control system designs to regulate the hydrogen flow rate traveling from a methane reformer to a proton exchange membrane fuel cell (PEMFC). The methane feed to the reformer was chosen as the throughput manipulator of a PI controller to modulate hydrogen production rates. A second PI control loop was designed to simulate catalyst temperature control. Similarly, Malik et al. (2020) simulated PI and PID closed-loops for hydrogen production and reformer temperature control.

Of the relevant experimental studies, selection of reactor temperature or hydrogen production as controlled variables is the norm for lab-scale PEM reforming. Control over proton migration rates, directly, is all but neglected. Cifuentes et al. (2023) employed a single PI controller with scheduled gains for high-pressure methanol reforming up to 12 bar. Andreasen et al. (2013) developed a cascading temperature controller to modulate reformer and burner temperatures via methanol and oxygen feed flows in a classical closed-loop control scheme. Likewise, Li et al. (2022) tested offset-free model predictive temperature control for a low-temperature PEMFC. Further efforts to automate PEM systems or similar thermo-electrochemical technologies are needed in order to properly control the dynamic electrochemical and thermal phenomena involved in these energy production processes.

Herein, a unique opportunity to observe and govern a transient, highly nonlinear methane reforming system with multilayered and cascading chemical interfaces is presented. Control engineering practice guides the automation of a single  $BaZr_{0.8-x-y}Ce_xY_yO_{3-\delta}$  protonic membrane reformer integrated into a watt-scale steam methane reforming process. To our knowledge, this work reports the first multi-input multi-output (MIMO) implementation of feedback control in an experimental PMR system. The results of the study contribute to the science of scale-up (Moore et al., 2024) and reaction engineering (Luterbacher et al., 2025) in a novel way by quantifying the emergent phenomena in dynamically-operated PMR systems and providing relevant controlled parameters for potential automation pathways.

## 2. Preliminaries

## 2.1. Notation

- A: G-cofactor matrix
- $C_i, C_i^{a,PMR}, C_i^{c,PMR}$ : Concentration of gas *i*, in anode (*a*) and cathode (*c*) chamber (mol m<sup>-3</sup>)
- *d*<sub>*ii*</sub>: Cofactor matrix element
- e(t): Error signal at time t (sccm or °C)
- *F*: Faraday's constant (C mol<sup>-1</sup>)
- $F_{i,0}^{a,PMR}$ ,  $F_{i,0}^{c,PMR}$ : Inlet molar flow rate of gas *i* to anode reformer chamber, and the cathode reformer chamber (mol s<sup>-1</sup>)
- Fex: Species extraction rate vector
- *G*, *G*<sub>*PMR*</sub>: General  $3 \times 3$  gain matrix,  $3 \times 3$  gain matrix structure for a PMR system
- *H R*: Hydrogen recovery ratio
- I: Membrane electrode assembly electric current (A)
- *K<sub>c</sub>*: PI controller proportional gain
- $q_{CH_4,0}$ ,  $q_{CH_4}$ : Initial feed methane flow rate, methane flow rate (sccm)
- q<sub>H2,0</sub>, q<sub>H2,a</sub>, q<sub>H2,c</sub>, q<sub>H2,dot</sub>: Initial hydrogen flow rate, anodic hydrogen flow rate, cathodic hydrogen flow rate, total hydrogen in the PMR system (sccm)
- $r_j$ : Rate of reaction *j* per kilogram of catalyst (mol (kg s)<sup>-1</sup>)
- $R_i$ : Rate of reaction  $j \pmod{s^{-1}}$
- *RGA*: Multi-dimensional  $(3 \times 3)$  and steady-state relative gain array for a general chemical process
- S/C: Anodic feed steam-to-carbon ratio



Fig. 1. (A) Protonic membrane materials, electrodes, and gas-phase flow paths. (B) Closed-circuit electron flow path from anode to cathode.

- *T*<sub>0</sub>: Initial reformer temperature (°C)
- T<sub>sp</sub>: Anodic bubbler PD controller temperature setpoint (°C)
- u,  $u_i$ ,  $u_{i,\infty}$ : Control input vector, control inputs, steady-state control inputs
- *V<sup>a,PMR</sup>*, *V<sup>c,PMR</sup>*: Volume of anodic reformer chamber, of cathodic reformer chamber (m<sup>3</sup>)
- W<sub>cat</sub>: Weight of nickel catalyst (kg)
- *x*<sub>Ar,*norxn*</sub>, *x*<sub>Ar</sub>, *x*<sub>H<sub>2</sub>,*a*</sub>: Argon mole fraction without reaction, argon mole fraction, anodic hydrogen mole fraction
- y,  $y_i$ ,  $y_{i,\infty}$ : Control output vector, control outputs, steady-state control outputs
- $\lambda_{ii}$ : Relative gain matrix element
- $\tau_I$ : Integral time constant of PI controller (min)

#### 2.2. Protonic membrane reformer unit

A protonic membrane reformer is a chemical processing unit that contains steam methane reforming reactions to transform methane fuel into energy-dense hydrogen gas while also facilitating the electrochemical transport of hydrogen across an ion-conducting ceramic membrane. As shown in Fig. 1, the mass and energy inputs to a protonic membrane reformer are, generally, methane, water vapor, furnace heat, and closed-circuit electrons. At the output of a PMR unit, hydrogen, carbon oxides, and solid carbon close the mass balance. Energy outputs include the dissipation of heat energy generated by Joule-heating and the additional heat energy generated by pushing protons against pressure gradients as hydrogen ions are transported from the anode reformer chamber to the cathode bulk stream. A nickel catalyst is also embedded on the surfaces of the membrane electrodes to lower the activation energies of the reforming reactions and simultaneously promote hydrogen oxidation or reduction.

Multiple hardware factors impose limitations on the ability of solid oxide ceramic reformers to produce, purify, and compress hydrogen gas. In addition to the challenges associated with the manufacturability of large-area ceramic membranes, there are intrinsic constraints on the optimization of the reaction kinetics and charge transport mechanisms in PMR reactors. For example, the hydrogen production rate in the anode chamber of a PMR unit directly depends on the dispersion of the active catalyst throughout the anode surface. The amount of active nickel surface sites on the anode is not only proportional to the catalyst weight, but it is also a function of how well the transport of mass and charge is optimized around the catalyst surface and within the anode catalyst layer. Facile kinetics for the SMR and WGS reactions are necessary but not sufficient, unless the membrane also has high proton conductivities to reform methane and separate hydrogen within an operating temperature window of 500 to 800 °C. Specifically for the cylindrical membranes utilized here, the characteristic mass transfer time of methane and water vapor molecules in the inner wall of the membrane must also be optimal for these reactants to diffuse radially to nickel surface sites on the anode. For this reason, the PMR unit in this work has an internal radius of 3.50 mm, an active anode surface area of 15.2 cm<sup>2</sup>, and supports a BZCY membrane of high conductivity developed by Coorstek (Fjeld et al., 2017; Clark et al., 2022). Solid oxide membranes made with BZCY electrolytes exhibit

virtually zero conductivity below 250 °C. However, the conductivity of these membranes increases from  $5.00 \times 10^{-3}$  to  $3.00 \times 10^{-2}$  S cm<sup>-1</sup> as local temperatures increase from 400 to 800 °C (Beyribey et al., 2021).

Given the aforementioned hardware constraints associated with protonic membrane reforming, the characteristic molecular diffusion time of methane molecules in the ceramic cylinder was approximated using a process simulator. The characteristic time scales of the SMR and WGS surface reactions were also calculated. Subsequently, the simulated rates of these two phenomena were compared using the second Damköhler number to avoid the selection of feed flow rates or reformer temperatures that would impose mass transfer limitations on the net hydrogen production rate. For a methane feed flow rate of 16.2 sccm in ambient pressure settings, the second Damköhler number is on the order of  $10^{-1}$ , mandating a kinetically-controlled operating regime for hydrogen production reactions (Hsu et al., 2024). This feed flow rate was selected as the initial methane input to the PMR system. Water saturation at the PMR electrode surfaces, regulated by the steam-to-carbon ratio in the inlet feeds, contributes to membrane conductivity and the net hydrogen production rate as well. Therefore, steam-to-carbon ratios higher than 2.00 in the PMR unit are essential for adequate electrochemical performance.

#### 2.3. Thermal and electrochemical protonic membrane reforming chemistries

Typical gas-phase chemistries that arise in protonic membrane reformers include the steam methane reforming, water-gas shift, electrochemical hydrogen oxidation, electrochemical hydrogen reduction, methane cracking, Boudouard, and carbon monoxide reduction reactions.

Steam methane reforming:

$$CH_4 + H_2O \Longrightarrow CO + 3H_2 \quad \Delta H_{298 K} = +206 \text{ kJ/mol}$$
(1)

The steam methane reforming reaction is a reversible, highly endothermic gas-phase reaction that is often characterized by a surface reaction mechanism. Molecules of methane and water vapor dissociate and react on catalytically active surface sites on the PMR anodic electrode to form carbon monoxide and hydrogen molecules. Nickel and other noble metals, like ruthenium or rhodium, can be used to catalyze the kinetic rates of this reaction to ensure near-equilibrium conversion of methane within reactor control volumes.

Water-gas shift:

$$CO + H_2O \Longrightarrow CO_2 + H_2 \quad \Delta H_{298 K} = -41 \text{ kJ/mol}$$
(2)

The water-gas shift reaction runs in series and parallel to the SMR reaction. For WGS kinetics and thermodynamics, carbon monoxide and water vapor also adsorb and dissociate on catalytically active surface sites where the molecules of each species are converted to hydrogen and carbon dioxide molecules. Unlike the SMR reaction, the WGS reaction is an exothermic equilibrium reaction that releases heat to the control volume surroundings, which is heat energy that may be consumed by unreacted methane molecules to further propagate the initial SMR reaction.

Methane Cracking:

$$CH_4 \rightleftharpoons C + 2H_2 \quad \Delta H_{298 K} = +75 \text{ kJ/mol}$$
(3)

Boudouard Reaction:

$$2 \operatorname{CO} \rightleftharpoons \operatorname{C} + \operatorname{CO}_2 \quad \Delta H_{298 \, K} = -172 \, \text{kJ/mol} \tag{4}$$

CO Reduction:

$$CO + H_2 \rightleftharpoons C + H_2O \quad \Delta H_{298 K} = -131 \text{ kJ/mol}$$
(5)

In addition to the SMR and WGS reactions, carbon formation reactions generate unwanted solid carbon byproducts in reformers. This requires the development of anti-coking catalysts and the use of operational conditions that limit carbon formation reactions. In the absence of such measures, solid carbon deposits on catalytically active surfaces, blocking reaction sites and thereby limiting reforming reaction rates and the overall conversion of methane to hydrogen (Meloni et al., 2020). Methane cracking is one such unwanted gas-phase reaction that splits methane molecules into solid carbon and hydrogen gas. The Boudouard reaction also generates solid carbon when two molecules of carbon monoxide are oxidized and reduced simutaneously. Whereas carbon monoxide in the Boudouard reaction acts as both an oxidizing and reducing agent, the carbon monoxide reduction reaction involves only the reduction of carbon monoxide to form solid carbon and water. These three reactions are described in the context of industrial applications because chemically-induced catalyst deactivation is a key disturbance in hydrogen production processes by way of steam methane reforming.

Hydrogen oxidation/reduction (HOR/HER):

$$H_2 \rightleftharpoons 2H^+ + 2e^- \quad E^\circ = 0.00 \text{ V (vs SHE)}$$
(6)

In PMR reactors, the separation of hydrogen relies on two reversible electrochemical transformations, namely, the hydrogen oxidation reaction on the anode and the hydrogen evolution reaction on the cathode. In Yuste-Tirados et al. (2023), the proposed electrochemical reaction mechanism for hydrogen oxidation at the anode envisions hydrogen gas diffusion from the anodic bulk stream to vacant nickel surface sites on the anode. At a catalytic surface site, hydrogen then dissociates into atomic hydrogen, and hydrogen atoms are thought to diffuse through the anode to the BZCY ceramic phase by nickel surface diffusion or nickel bulk diffusion. Once the hydrogen atoms reach the BZCY ceramic phase, the redox charge transfer splits the hydrogen atoms into protons and electrons. When a strong potential gradient exists from the anode to the cathode, proton migration through the BZCY electrolyte becomes the dominant transport process. The electrical potential is therefore a driving force that allows protons to migrate against the pressure gradient from an elevated cathode chamber pressure. As electrons carry negative charges from the anode to cathode, the negative charges attract the protons and move these positive ions against the oncoming pressure gradient. Once protons arrive at the interface of the BZCY electrolyte and cathode surface, the protons are reduced back into atomic hydrogen on cathodic nickel surface sites where the hydrogen atoms reform hydrogen gas molecules and diffuse into the cathodic bulk stream.

#### 2.4. Experimental PMR system

The experimental PMR system examined in this work is both novel and unique for an academic setting wherein study of a hydrogen production system provides an abundance of control volumes and interfaces to be defined, characterized, analyzed, and modeled. Relevant control volumes defined for the entire PMR system are the anodic bubbler, the cathodic bubbler, the anode reformer chamber, and the cathode reformer chamber. Between these volumes, there exists a series of interfacial phenomena at the anode surface, the BZCY-electrolyte solid phase boundaries, and the cathode surface.

The overall mass balance for the PMR system includes six feed streams as well as two product streams for the anodic effluent and the purified hydrogen product stream (Fig. 2A). There are eight overall energy inputs to the PMR system: the enthalpies of the six feed streams, furnace heat, membrane electrical energy, the anodic bubbler heater, the cathodic bubbler heater, the energy stored in the inlet methane and hydrogen molecular bonds, and the heat supplied by upstream and downstream tube heaters. The enthalpies of the anodic and cathodic effluent streams, the enthalpies of reaction, heat of hydrogen separation, heat of hydrogen compression, external heat losses to surroundings, and the energy stored in unreacted or synthesized fuels comprise the energy outputs of the PMR system and close the overall energy balance (Fig. 2B).

## 2.5. Significant process disturbances

A disturbance can be classified as a transient, periodic, or permanent deviation in the state of a system due to external or internal perturbations. Feedback control loops mitigate these perturbations by reacting to downstream process information within process-specific constraints or limits. Depending on the time scale and magnitude of known disturbance phenomena, control loops can be designed and tuned accordingly to bring a process to the desired states of operation. The effectiveness of each control loop is improved when significant process disturbances are accounted for in controller design.

In preliminary PMR experiments, key disturbances were identified, including temporal changes in catalyst activity, stream pressure oscillations, cell voltage spikes, and irregularities in the cathodic effluent gas flow. Irreversible shifts in catalyst performance arise after a few hours of reformer operation, and periodic shifts above and below the temperature setpoints of the bubbler units induce a  $\pm 0.200$  bar stream pressure oscillation in both the anode and cathode reformer chambers. Drops in the cathodic stream pressure, due to upstream pressure oscillations, can momentarily block hydrogen flow in the cathodic effluent if the stream pressure dips below the back pressure regulation setpoint. In such cases, the hydrogen flow rate through the sensor is null. Voltage spikes are an additional source of disturbance that occur when the BZCY electrolyte becomes dehydrated or the anode reformer chamber is devoid of hydrogen, with either condition causing a sudden increase in cell resistance.

## 3. Control problem formulation and controller design

## 3.1. Overview

Process control theory frames effective control architectures that are able to continuously achieve process-specific control objectives. Process engineers employ this framework to develop closed-loop control algorithms to achieve these desired objectives. For a highly-complex, nonlinear chemical process, controller design benefits from a complimentary combination of theoretical control protocols with the physical understanding of a process formed during empirical investigations. In this section, control objectives are put forth for the experimental PMR system to identify control degrees of freedom (CDOF) that may achieve process-specific control objectives, to select manipulated variables, and to determine process controller interactions a priori.

#### 3.2. Control objectives

High-temperature thermo-electrochemical processes must contain control systems that protect process engineers and the local environment. Accordingly, an essential experimental metric is the safety of the process during transient operational states, which can be quantified by the internal reactor temperature, pressure, and cell voltage. Controller effectiveness is a secondary objective used to guide controller designs that reach process variable setpoints within reasonable time scales, maintain the desired setpoints over time, and maintain controllability when in the presence of significant process disturbances. Time-tosetpoint, time-at-setpoint, and average setpoint error, are measures for the secondary objective. The tertiary objective, and main goal of



Fig. 2. Qualitative mass (A) and energy (B) balances for a PMR system. The operational domains for experimental process control are listed as well. Solid arrows represent continuous flows of mass, and dashed arrows represent continuous flows of energy in the form of fuel, heat, or electricity.

this work, is to demonstrate that the developed control architecture functionally adapts the total hydrogen production rate during setpoint tracking for dynamical use cases. One such case considers a renewable electric power source, like a wind turbine, that generates electricity in an inconsistent manner. The control architecture must safely and effectively transition the hydrogen separation rate and total hydrogen production rate in response to input power fluctuations while maintaining the initial steam-to-carbon ratio.

Therefore, the explicit objectives of this process control design are:

- 1. Control actions must be bound by upper and lower operational limits for temperature, pressure, electric current, and methane feed flow rates.
- An effective control design will achieve and maintain all control variable setpoints with minimal error, minimal time elapsed, and adequate controller stability.
- 3. As the total hydrogen production rate is adapted, the control system will effectively transition the process between setpoints by actuating safe and effective control actions.

## 3.3. Selection of manipulated and controlled variables

Control degrees of freedom analyses elucidate the number of ways a process engineer can manipulate the inlet and outlet streams of a control volume or interface. This number is constrained to the number of independent streams influenced by modulating process parameters. Taking an unimolecular irreversible reaction inside of a plug flow tubular reactor as an example, the state of the feed stream may be regulated by changing mass flow rates through a variety of actuators. Likewise, the state of the effluent stream is bound to the temperature and pressure of the internal volume of the plug flow reactor. Thus, there exist two control degrees of freedom to actuate this theoretical reactive unit in order to execute all control objectives associated with the process.

Control degrees of freedom must be also specified in ways that establish control over the targets of a process. Extending a degrees of freedom analysis to the PMR system requires the flowsheet analysis provided in Fig. 3. In this figure, each process stream represents a control degree of freedom if and only if it can be controlled by an independent parameter and there is containment of mass inventory in the volume of interest. Restrained streams have imposed constraints in that the inlet mass flow necessarily equates to the outlet mass flow, as in mass flux through interfaces (Stream 3 and Stream 4 in Fig. 3). The PMR system in consideration has an anodic bubbler with a liquid-gas material inventory and two process streams, each of which is independently controlled by thermodynamic or transport parameters. The PMR unit, on the other hand, is configured with anodic and cathodic streams plus two flux streams defined by the mass transfer of protons through the BZCY electrolyte. The dependent process stream in the PMR unit is  $F_5$  (Fig. 3), which is always exactly equal to  $F_4$ . Though there are five independent streams within the PMR control volume, Stream 2 is redundant. In other words, placing a controller at the bubbler exit and at the anodic feed of the PMR would result in the same control action and only one controller is needed as a result. Thus, four control degrees of freedom exist for the PMR unit, and two degrees are available to control the anodic bubbler.

The kinetic rates of steam methane reforming are nonlinearly influenced by the steam-to-carbon ratios, reformer temperatures, and the axial composition of gaseous products. To regulate production rates, any controller design for this process must regulate the hydrogen separation rate, the availability of system-wide hydrogen, and the steam-to-carbon ratio. These are the controlled variables for the design. Identification of independently controllable mass flows may also be coupled with economic insight to select manipulated and controlled variables. Stream 7 contains the pure and compressed hydrogen product, which is the target variable and value-added product of the PMR system. Stream 6 also contains hydrogen that can be subsequently separated. Taking the locations of process actuators and target variables into account, Stream 1, Stream 2, and Steam 4 were chosen to directly enhance the production rate of hydrogen in the PMR system.

Considering process stream compositions and other thermodynamic parameters, there exists a range of variables that may be manipulated



Fig. 3. Flowsheet-oriented control degrees of freedom for the proposed control volumes in the PMR system control architecture.

to modulate the aforementioned controlled variables, and physical intuition combined with an RGA provides a basis for coupling these control inputs and outputs. Based on the work of Field et al. (2017), the potential differential across membrane electrodes is the dominant driving force for hydrogen separation through a protonic membrane reformer. Given the electromotive force can be directly adjusted by a potentiostat, applied electric current is chosen as the manipulated variable for the first controller that regulates hydrogen separation rates. The second controlled variable, defined here as the total, or global, hydrogen flow in the system, mainly depends on the limiting reactant of the SMR reaction, which is the methane composition in the anodic feed mixture. For the third control loop, the ratio of steam to methane in Stream 2 (Fig. 3) can only be changed by adjusting the internal liquid temperature of the anodic bubbler. The control pairings for three control loops are, therefore: the membrane electrode assembly (MEA) electric current, the methane feed flow rate, and the anodic bubbler temperature to control hydrogen separation, hydrogen production, and the steam-to-carbon ratio, respectively. This design hypothesis underspecifies the control system and allows for three additional control degrees of freedom should they be needed for after-the-fact optimization efforts.

## 3.4. Relative gain array formulation

Multi-input multi-output control loops often contain manipulated input variables that directly or indirectly impact the controlled variables in adjacent loops. To determine an optimal control scheme, a relative gain array (RGA) can be constructed as an analytical metric put forth to characterize control loops and determine effective operating regimes for a complex system a priori. To construct a relative gain array, a steady-state gain matrix is assembled that relates each manipulated variable to every controlled variable for an open-loop process. Steady-state RGA matrices may be derived from experimental data or predictive process models to ensure the appropriate pairing of each manipulated variable to a corresponding target variable.

For a general steady-state gain array:

$$y = Gu \tag{7}$$

*y* is an *n*-dimensional vector containing all controlled, or output, variables. The output vector *y* is equal to the matrix–vector product of the  $n \times n$  dimensional *G* matrix and *n*-dimensional *u* vector that contains all manipulated input variables. In the previous subsection, three manipulated variables were chosen to control the hydrogen separation rate, the hydrogen production rate, and the S/C ratio of the PMR process.

Thus, vectors u and y have three dimensions, and G is a  $3 \times 3$  matrix. Specifically, the y and u vectors can be expressed as follows:

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix}$$
(8)  
$$\mathbf{u} = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix}$$
(9)

The G matrix is referred to as the steady-state gain matrix because it maps each input to a steady-state output through the use of partial derivatives. Analytical or empirical functions that capture steady-state behavior as a function of the manipulated variables can be used to find rates of change in the steady-state outputs under different operational conditions.

$$\boldsymbol{G} = \begin{bmatrix} \frac{\partial y_{1,\infty}}{\partial u_1} & \frac{\partial y_{1,\infty}}{\partial u_2} & \frac{\partial y_{1,\infty}}{\partial u_3} \\ \frac{\partial y_{2,\infty}}{\partial u_1} & \frac{\partial y_{2,\infty}}{\partial u_2} & \frac{\partial y_{2,\infty}}{\partial u_3} \\ \frac{\partial y_{3,\infty}}{\partial u_1} & \frac{\partial y_{3,\infty}}{\partial u_2} & \frac{\partial y_{3,\infty}}{\partial u_3} \end{bmatrix}$$
(10)

where  $y_{i,\infty}$  are the outputs of Eq. (7) at steady-state. In order to construct the RGA matrix, the inverse transpose of the steady-state gain matrix is calculated from multiplying the transpose of the cofactor matrix of *G*, defined below as *A*, and the scalar-inverse of the determinant of *G*, as follows:

$$\boldsymbol{R} = (\boldsymbol{G}^{-1})^T = \frac{1}{det(\boldsymbol{G})} \boldsymbol{A}^T$$
(11)

$$\mathbf{A} = \begin{bmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \end{bmatrix}$$
(12)

In Eq. (11), **R** is defined as the inverse transpose of the steady-state gain matrix. In Eq. (12), **A** is the cofactor matrix made up of  $d_{ij}$  cofactors. From these terms, the steady-state RGA is calculated following Eq. (13) to give the  $\lambda_{ij}$  values in Eq. (14) below:

$$RGA = \lambda(G) = G \odot (G^{-1})^T$$
(13)

$$RGA = \begin{bmatrix} \lambda_{11} & \lambda_{12} & \lambda_{13} \\ \lambda_{21} & \lambda_{22} & \lambda_{23} \\ \lambda_{31} & \lambda_{32} & \lambda_{33} \end{bmatrix}$$
(14)

where RGA is the relative gain array matrix that is a function of G based on the element-wise product ( $\odot$ ) of G and R. The normalized

elements of the RGA defined as  $\lambda_{ij}$  are the relative gains for the steadystate process and predict the degree of effectiveness for the control loop pairings.

Finally, the steady-state gain array for the PMR system is defined as  $G_{PMR}$  in Eq. (15):

$$\boldsymbol{G}_{\boldsymbol{PMR}} = \begin{bmatrix} \frac{\partial q_{\mathrm{H}_{2},cath}}{\partial I} & \frac{\partial q_{\mathrm{H}_{2},cath}}{\partial q_{\mathrm{CH}_{4}}} & \frac{\partial q_{\mathrm{H}_{2},cath}}{\partial T_{sp}} \\ \frac{\partial q_{\mathrm{H}_{2},total}}{\partial I} & \frac{\partial q_{\mathrm{H}_{2},total}}{\partial q_{\mathrm{CH}_{4}}} & \frac{\partial q_{\mathrm{H}_{2},total}}{\partial T_{sp}} \\ \frac{\partial (S/C)}{\partial I} & \frac{\partial (S/C)}{\partial q_{\mathrm{CH}_{4}}} & \frac{\partial (S/C)}{\partial T_{sp}} \end{bmatrix}$$
(15)

where  $G_{PMR}$  is composed of all possible combinations of the chosen manipulated and controlled variables. In  $G_{PMR}$ , the hydrogen in the cathode reformer chamber only depends on the electric current passing through the membrane, resulting in  $\frac{\partial q_{\text{H}_2,cath}}{\partial q_{\text{CH}_4}} = \frac{\partial q_{\text{H}_2,cath}}{\partial T_{sp}} = 0$ . Similarly,  $\frac{\partial (S/C)}{\partial I} = 0$  is assumed since S/C ratio is independent of the electric current.

#### 3.5. State estimator for RGA analysis

In Cui et al. (2024a), a nonlinear state estimator for the PMR system considered in this work was derived and experimentally-validated. The estimator, which adequately predicts steady-state mass and energy distributions, is now adopted to calculate  $G_{PMR}$  and carry out the *RGA* analysis.

The steady-state model for the concentrations of all gaseous species in the anode chamber of the PMR is developed as follows:

$$0 = \frac{F_0^{a,PMR} + R - q^{a,PMR} C^{a,PMR} - F_{ex}}{V^{a,PMR}}$$
(16)

where the steady-state of all species concentrations is captured by  $C^{a,PMR}$ , as follows:

The steady-state model for gas species concentrations in the cathode is given by the following equation:

$$0 = \frac{1}{V^{c,PMR}} \left( F_{\mathbf{0}}^{c,PMR} - q^{c,PMR} C^{c,PMR} + F_{ex} \right)$$
(18)

$$\boldsymbol{C}^{c,PMR} = \begin{bmatrix} \boldsymbol{C}_{\text{H}_{2}\text{O}}^{c,PMR} \\ \boldsymbol{C}_{\text{H}_{2}}^{c,PMR} \end{bmatrix}, \quad \boldsymbol{F}_{\boldsymbol{0}}^{c,PMR} = \begin{bmatrix} F_{\text{H}_{2}\text{O},0}^{c,PMR} \\ F_{\text{H}_{2},0}^{c,PMR} \end{bmatrix}, \quad \boldsymbol{F}_{ex} = \begin{bmatrix} 0 \\ \frac{I}{2F} \end{bmatrix}$$
(19)

where the steady-state of all species concentrations is captured by  $C^{c,PMR}$ . Tuning  $W_{cat}$  in **R** of Eq. (17) to fit experimental steady-state data permits use of Eqs. (16) and (18) to calculate the total hydrogen production rate gains.

#### 4. PMR reactor construction, digitalization and control

#### 4.1. Fabrication: PMR reactor assembly

The PMR anodic feed stream was created using nickel tubing. To assemble the nickel tube apparatus, a 3/16 inch customized tee was secured to a 1/4 inch stainless steel anodic feed stream tube. Separately, a meter of nickel tubing (Goodfellow, OD: 4.5 mm, ID: 3.15 mm) was swaged into a 3/16 inch tee. Spacing for the upstream copper current collector was measured to fit within the furnace dimensions. On the opposite side of the upstream current collector, a 3/16 inch nut and ferrule were swaged into place, facing away from the adjacent 3/16 inch nut. Following this, a 1/4 inch reducer fitting was attached and swaged with a 1/4 inch nut and ferrule set. The 1/4 inch nut was further fastened to a 1/2 inch reducer, which screwed onto a half inch tee with a 1/4 inch outlet for the anodic effluent, completing the nickel tube assembly.

The second phase of the assembly process required the wrapping of the MEA (CoorsTek) with 30 inches of oxygen-free copper wire (Goodfellow, 0.25 mm dia) using a twist-and-turn technique (Fig. 4), ensuring a secure connection between the wire and the nickel tube. Nickel wool was also packed into the membrane for increased electrical contact between the MEA electrodes. To install the nickel wool, it was first separated into thin, hair-like strands, which were formed into 1 cm diameter disks before being packed down to the end of the membrane. Two additional wool disks were packed into the membrane, followed by a 3 cm long, loosely-packed nickel wool spool with a cylindrical geometry. This formed a sufficient electrical contact layer between the nickel tubing and anode that was essential for membrane conductivity and performance. The axial length of the nickel tube was further adjusted to reach the nickel wool near the MEA cap for proper fitting. To connect the nickel tube assembly with the MEA, PTFE ferrules were connected to a 1/2 inch tee with a 1/2 inch nut and 1 inch reducer. These components were stacked in the following order, from bottom to top; 1/2 inch nut for the 1/2 inch tee, 1/2 inch nut for the 1 inch reducer, and the 1 inch reducer itself. Then, the alumina riser was slid over the nickel tube. The 1/2 inch nut connected to the 1/2 inch tee was swaged into place, and turned once; the complete swage was performed later in the reactor setup procedure.

Once the nickel tube assembly and membrane were connected, a copper rod was wired and attached to the MEA (Fig. 4). With the main assembly placed upright in a vice, the copper rod was positioned just above the membrane cap leaving a 1.50 cm gap between the copper rod and MEA cap. The excess copper wire was wrapped around the copper rod using the same twist-and-turn technique used during the copper wire threading process. After the first layer was secured, a second layer of copper wire was added with the new braids spaced farther apart to accommodate the additional wire.

Next, the entire assembly was placed inside a tube furnace (Thermolyne<sup>®</sup> 21100 Tube Furnace). The copper-rod-side of the main assembly was positioned on the leftmost side of the furnace. The assembly was pushed through the reactor until the copper rod cleared the furnace on the rightmost side. Once in position, the copper rod was gently pulled through a 1 inch tee, 1 inch reducer, and 1/4 inch nut, after which it was swaged with a 1/4 inch nut-ferrule set. The 1 inch tees were hand-tightened and the gas outlet and input lines were finger-tightened to temporarily secure the membrane in place.

Before reactor operation, the assembly underwent a series of final fastenings and checks for proper system integration. First, the bump stop from the 1/8 inch reducer was removed using a 1/16 inch drill bit. The 1/16 inch end of the 1/8 inch reducer, connected to the 3/16 inch reducer, was slid down the length of a K-type thermocouple (DwyerOmega, OD: 1/16 inch). The thermocouple was subsequently inserted into the 3/16 inch tee, ensuring it touched the packed-nickel wool inside of the membrane. The 3/16 and 1/8 inch reducers were swaged to the 3/16 inch tee after securing the thermocouple in the



Fig. 4. (A) Reformer parts and MEA (Richard, 2023). (B) Anodic feed section of the PMR unit prior to the installation of current collectors and fiberglass insulation. (C) PMR unit prior to the installation of electrical leads and fiberglass insulation. (D) PMR system in UCLA laboratory. (E) CoorsTek BZCY membrane with braided copper wire.

reformer. These connections were tightened with one-and-one-quarter turns. A two-wrench method was employed to fasten all fittings for gas-tight seals using Swagelok<sup>®</sup> installation protocols. After the assembly was tightened, the entire system was pressurized with helium to 5.00 bar, and a leak test was conducted. Any points of connection with gas leaks were further tightened. Finally, electrical heating tape (BriskHeat Insulated Heat Tape) was applied around the external components of the assembly, followed by insulation to ensure proper temperature management during system operation.

### 4.2. Digitalization: Sensors and actuators

The network of chemical and physical processing units in the PMR system necessitated the use of advanced sensing techniques to collect real-time data from the hydrogen production machinery. This data was contextualized to quantify the thermodynamic states of all system units over time, providing a way to monitor or calculate all relevant process variables for system characterization, reactor modeling, and control. In order to contextualize raw data, transmitted in periodic voltage or amperage signals, a CompactRIO device was used (National Instruments). A CompactRIO is a modular computational device that serves as an analog-to-digital signal interface. The digital voltage or amperage signals transmitted by the CompactRIO to the system computer were transformed from electrical values to pressure or temperature values by way of mathematical formulas.

All inlet feeds were controlled by mass flow controllers (Brooks Instrument SLA5850 Series) for precision control of gas feed volumetric flow rates at elevated system pressures. The mass flow controllers were paired with a power supply (Brooks Instrument 0254 Series) and display that communicated directly with the PMR system computer via RS-232 serial communications cables. Within the LabVIEW software, the BrooksDLL library was used to initialize and establish continuous incoming and outgoing data transmission with all four mass flow controllers.

Two steam cabinets housing the anodic and cathodic bubbler equipment were place after the mass flow controllers. The dry anodic feed was bubbled through liquid water in a 1 L stainless steel cylinder. A wet mixture of the gaseous inlet species was formed in the anodic bubbler. On the cathode side of the system, the only gas species in the dry feed was hydrogen. The dry hydrogen gas was also bubbled through liquid water, albeit in the cathodic bubbler, and the cathodic bubbler outlet was a mixture of hydrogen gas and water vapor. The stainless steel cylinders of the bubblers were wrapped in heavy-insulated electrical heating tape that supplied heat energy to the internal liquid volumes via Joule-heating and subsequent heat conduction through the stainless steel cylinder. The heating tape was electrically insulated to avoid electric current leaks through the cylinders or system piping. To control the amount of electric energy that was transformed into heat energy, the electrical heating tapes were connected to temperature actuators (Omega CS8DPT Universal Benchtop Controller). These actuators modulated the voltage to the electrical tapes and received temperature feedback information from two thermocouple probes (DwyerOmega, OD: 1/16 inch) that were swaged into both bubblers. The bubbler actuators used an RS-232 communication interface that established communications to and from the PMR system computer. These signals were contextualized within the LabVIEW software and user interface via the Omega Platinum MBus protocol, which allowed read and write privileges to the Omega temperature actuators. Each bubbler was also equipped with a pressure gauge and pressure transducer to provide analog and digital pressure readings in either unit. Pressure transducers (DwyerOmega PX359-1KGI) and vented cables (DwyerOmega M12) were used for this purpose. Each transducer transmitted analog current signals to an eight-channel Compact Rio module (National Instruments 9203 Module, ±20 mA). The module served as a port for analog-todigital signal conversion on a per-second basis. The digitalized pressure transducer data was further contextualized in LabVIEW using a Field Programmable Gate Array (FPGA) to develop a local application that converted electrical data from the transducers into relative pressure values.

The PMR unit also contained thermocouple probe (DwyerOmega, OD: 1/16 inch) to measure the internal gas temperature in the anode chamber near the MEA cap. The probe had an ungrounded, K-type junction with an iconel sheath to minimize electrical noise interference, to prohibit electrical current leaks to surrounding hardware, and to generate fast signal response times (Fig. 5A). The PMR thermocouple wires were fastened to a four-channel Compact Rio module (National Instruments 9211 Module,  $\pm$ 80 mV) to transmit and convert analog voltage signals into digital signal values. The digitized voltage signals were subsequently contextualized in LabVIEW using an FPGA application to convert voltage data into temperature readings on a per-second basis. Pressure transducers (DwyerOmega PX359-1KGI) and vented cables (DwyerOmega M12) were also used to measure the pressures of the reformer feeds (Fig. 5B).

A potentiostat (Metrohm PGSTAT302N and 20A Booster) in galvanostatic mode was used to measure and control the flow of electrical current through the closed-circuit of the PMR unit. The potentiostat



Fig. 5. (A) K-type thermocouple with ungrounded junction. (B) Pressure transducer with strain guage detector.

Table 1										
Tuning parameters	for all	three	ΡI	controllers	in	the	MIMO	control	architecture	•
PI Controller		K					K <sub>c</sub> Uni	it	$\tau_I$ (	min]

PI Controller	$\mathbf{K}_{c}$	$K_c$ Unit	$\tau_I$ (min)
1	$2.00 \times 10^{-2}$	A sccm <sup>-1</sup>	1.00
2	$1.00 \times 10^{-3}$	-	0.12
3	$1.00 \times 10^{-1}$	-	0.13

was equipped with onboard analog-to-digital signal converters that transferred data to and from the PMR system computer. Data contextualization was performed with the Autolab Software Development Kit in LabVIEW to establish read and write protocols for the galvanostatic and potentiostatic operating procedures that enable full control of the potentiostat and booster module.

Back pressure regulators (Equilibar LF-Series) managed the upstream and downstream system pressures in the cathodic and anodic streams. Electronic pilot-pressure controllers (Equilibar EPR-1000) allowed users to set the pressure on either side of the system directly through the pilot controllers. Essentially, the pilot pressure was used to apply force to a flexible elastomer that allowed gas flow through the back pressure regulator once the process pressure reached the pilot pressure setpoint. The pressurization rate on either side of the system was therefore determined by the magnitude of the feed flow rates.

Quantification of the anodic effluent gas composition was conducted with a gas chromatography device (Agilent 7890B Gas Chromatograph) equipped with a thermal conductivity detector (TCD). The TCD columns were used to measure the anodic hydrocarbon product distribution and anodic hydrogen. The device was run in sequencing mode through the OpenLab ChemStation software in 18 min sampling intervals with a 15 min delay time. An automation algorithm was developed to integrate GC peak signals and convert GC peak areas to mole-percent compositions. These values were later transformed into standardized volumetric flow rates using Argon as a tracer element. The algorithm automatically calculated volumetric flow rates at the conclusion of each GC injection and exported the flow rate data to a custom LabVIEW software application developed for the PMR system.

Pure hydrogen in the cathodic effluent was quantified with a digital mass flow meter (Alicat M Series). The flow sensor was connected to the PMR system computer via RS-232 serial communications protocols. Within LabVIEW, read privileges were established with the flow meter using a virtual instrument driver, which stored flow rate measurements on a per-second basis. The complete process diagram including sensors, actuators and controllers is shown in Fig. 6.

#### 4.3. PMR control architecture: Closed-loop system

The process in Fig. 7 presents three outputs  $(y_1, y_2, y_3)$ , three inputs  $(u_1, u_2, u_3)$ , and an array of feedback measurement devices. The hydrogen separation rate and total hydrogen flow rate, in the real system, depend on all three inputs. Conversely, the anodic bubbler is solely regulated by the methane feed flow rate and bubbler temperature. The third loop expresses the uppermost layer of the S/C ratio controller, as there is an underlying PD controller installed within the anodic bubbler unit in the actual process.

#### 4.4. Controller tuning methods

Table 1 documents the final PI tuning parameters in each of the three process control loops. Generally, all three PI controllers were detuned to have slower closed-loop responses to deal with input constraints and multivariable coupling. Controller 1 was initially tuned using the Cohen-Coon PI algorithm. A dead time of 1.00 s along with a 2.00 s process time constant was observed during open-loop experimentation. The Cohen-Coon predictions for  $K_c$  and  $\tau_I$  were  $6.72 \times 10^{-2}$  A sccm<sup>-1</sup> and  $1.97 \times 10^{-1}$  min. Ultimately, the control parameters were adjusted to decrease the controller sampling time to avoid rapid Jouleheating of the Ni-BZCY electrodes. Controller 3 was tuned twice, using the Ziegler–Nichols heuristic method for the PD sublayer controller and trial-and-error for the PI upper layer in LabVIEW. The proportional and derivative bands for the PD sublayer were set to 8.5% and 10%, respectively.

Limited by infrequent and delayed sensor feedback time, parameters in Controller 2 were approximated by the experimentally-validated lumped-parameter model using a Ziegler–Nichols approach. In particular, the ultimate gain ( $K_u$ ) was obtained by setting integral and derivative terms to zero. After that, the  $K_c$  and  $\tau_I$  were designed based on the empirical PID parameter table from Hang et al. (1991).



Fig. 6. System P&ID to display: piping flow paths, piping dimensions, chemical processing units, actuators, sensors, controllers, and electrical pathways.



Fig. 7. Representation of the closed-loop MIMO control system for the PMR system using three feedback controllers (PI).



Fig. 8. Automatic setpoint logic for PI Controller 1.

#### 5. Real-time operational calculations

#### 5.1. PI control algorithm

The PI control algorithm implemented in LabVIEW is given by:

$$u(t) = K_c \left( e(t) + \frac{1}{\tau_I} \int_0^t e(\tau) \, d\tau \right)$$
(20)

where  $K_c$  and  $\tau_I$  are the proportional gain and integral time constant for a single PI controller. The proportional gain impacts control actions in proportion to the output error; the output error in deviation form is defined as  $e(t) = y^*(t) - y(t)$  at sampling instant t where  $y^*(t)$  is the desired setpoint value for the output. To improve the accuracy of control actions, and to minimize setpoint offset, the integral term accumulates the system output error over time; the accumulation of error in deviation form can be captured by  $E(t) = \sum_{z=0}^{t} e(z)$  at instant t, hence the integral term in Eq. (20) for absolute error. Both  $K_c$  and  $\tau_I$ are tuned so that the controller moves the process towards the desired output state. PI Controller 1 and Controller 3 were programmed for per-second sampling times. PI Controller 2 was also programmed for a per-second controller sampling time, though the measurement feedback sampling time was 18.0 min.

#### 5.2. Controller 1: Setpoint dynamic compensation

Controller 1 was programmed with an automatic setpoint layer to adaptively change the hydrogen separation rate setpoint as a function of the hydrogen production rate. This type of dynamic setpoint compensation helps to stabilize hydrogen transport in the anode chamber of the reformer by preventing total dehydrogenation of the anode. The setpoint generator algorithm is analogous to an industrial operational control loop layer and ensures some hydrogen remains in the reformer to limit resistance spikes during high-temperature electrolysis and to limit carbon formation reactions. Fig. 8 provides the Controller 1 operational logic that generates the hydrogen in the system, as calculated from the most-recent GC injection.

#### 5.3. Hydrogen recovery

Hydrogen recovery is terminology for the portion of purified hydrogen in the PMR system, and it is mathematically defined as follows:

$$HR = \frac{F_{H_{2,c}} - F_{H_{2,0}}}{F_{H_{2,a}} + F_{H_{2,c}} - F_{H_{2,0}}}$$
(21)

#### 5.4. Total hydrogen (global) and measurement uncertainty

The total hydrogen flow rate is calculated as follows. First, we define:

$$q_{tot,a} = q_{0,a} \times \frac{x_{\text{Ar},norxn}}{x_{\text{Ar},t}}$$
(22a)

Note that  $x_{Ar,norxn}$  is a function of the control time since the initial mole fraction of Ar in the absence of a chemical reaction changes with the feed flow rate of methane. Then, we have:

$$q_{\mathrm{H}_{2,a}} = q_{tot,a} \times x_{H_{2,a}} \tag{22b}$$

$$q_{\rm H_2,tot} = q_{\rm H_2,a} + q_{\rm H_2,c} + q_{\rm H_2,0} \tag{22c}$$

The appreciation of error propagation chains that start with sensor uncertainty is a critical factor influencing the performance of a control system. Each control action is calculated in response to a real-time measured or estimated process variable that is determined with some type of sensing technology. Sources of measurement error and uncertainty for total system hydrogen amounts are described, defined, and quantified, in the following relation:

$$\Delta q_{\rm H_2,tot} = \sqrt{\left(\frac{\Delta x_{\rm H_2}}{x_{\rm H_2}}\right)^2 + \left(\frac{1.2}{q_{\rm H_2,tot}}\right)^2 + \left(\frac{0.006 \cdot q_{\rm H_2,c,avg}}{q_{\rm H_2,c}}\right)^2}$$
(23)

Eq. (23) considers the uncertainties of the cathodic flow meter, the Argon tracer flow rate uncertainty used in calculating the total hydrogen flow rate, and the GC calibration uncertainty for the anodic hydrogen mole-percent composition.



Fig. 9. Steam methane reforming in the absence of electrochemical hydrogen separation. (A) Steady-state anodic gas compositions at 1.00 bar. (B) Steady-state anodic gas compositions at 3.15 bar. Error bars represent the propagation of the standard deviations and average uncertainties of five GC measurements at each reformer temperature.

#### 5.5. Steam-to-carbon ratio

The steam-to-carbon ratio can be calculated as follows. First, we calculate:

$$q_{\text{steam},a,0} = (q_{\text{CH}_{4},a,0} + q_{\text{H}_{2},a,0} + q_{\text{Ar},a,0}) \times \frac{P_{\text{steam},a,0}}{P_{a,\text{bubbler}} - P_{\text{steam},a,0}}$$
(24a)

where the steam partial pressure can be calculated using the Antoine equation:

$$\log_{10} |P_{\text{steam},a,0}| = A - \frac{B}{T_{a,\text{bubbler}} + C}$$
(24b)

where A, B and C are constant parameters for empirical water vapor pressure curves as a function of temperature (de Nevers, 2012). This back calculation of vapor pressure from the anodic bubbler temperature leads to the determination of the steam-to-carbon ratio as follows:

$$S/C = \frac{q_{\text{steam},a,0}}{q_{\text{CH}_{4,a,0}}}$$
 (24c)

## 6. Results

#### 6.1. Steady-state thermal reforming and model validation

Ambient and elevated pressure results for steady-state thermal reforming, in the absence of hydrogen separation and an applied electric current, are shown in Fig. 9. The experimental data fits to the spatiallyuniform CSTR model in Cui et al. (2024a,b), and the average model error for all species at either pressure was 0.95 sccm. Model errors were minimized at 66.0 mg and 13.0 mg catalyst weights for the 1.00 bar and 3.15 bar datasets, respectively. Contrary to expectation, the experimental methane conversion at 3.15 bar exceeded 1.00 bar conversion in the 550 to 650 °C temperature range (Fig. 9B). Hydrogen compositions throughout the steady-state operating regime closely follow the lumped-parameter model predictions, however. It was also observed that hydrogen production rates fell by over 15.0 sccm at all 3.15 bar steady-state temperatures due to the thermodynamic impact of a pressure delta on the state of the system and any changes in the activity of the anode catalyst. When the pressure-driven equilibria shifts in the SMR and WGS reactions occurred, the carbon oxide selectivity towards carbon dioxide was 0.457 at 737 °C and 3.15 bar, yielding a slight amplification of the carbon dioxide selectivity at higher system pressures. The change in the catalytic activity parameter as a function of pressure, in order to match experimental results with the model, indicates a change in the actual catalytic activity of the anode or a plant-model mismatch for changes in the system pressure. Given the empirical nature of data generation for kinetic model parameters (Schmidt, 2005), validation of the spatially-uniform reaction engineering model under different steady-state conditions was needed to determine the appropriate kinetic parameters for the RGA analysis.

## 6.2. Dynamic thermal reforming with electrochemical hydrogen separation

Using a  $10^{-1}$  A min<sup>-1</sup> electric current sweep rate across the MEA caused a transient response in the flow rates and compositions of both the cathodic and anodic reformer streams. Fig. 10 shows outlet species compositions in the anodic and cathodic effluents and reveals the temporal behavior of the system during electrochemical separation processes. Around 150 min, the current sweep was initiated and the hydrogen separation rate into the cathodic bulk stream followed a rate of  $\frac{I}{2F}$ , as confirmed by the experimental results provided in Fig. 10. Meanwhile, the total hydrogen production rate increased to 69.9 sccm at 9.00 A of electric current (or 0.592 A cm<sup>-2</sup>). The maximum separation rate of hydrogen gas through the protonic membrane was



**Fig. 10.** Transient experimental results induced by an electric current sweep rate of  $8.00 \times 10^{-3}$  A (5 s)<sup>-1</sup>. (A) Anodic hydrogen generation rates and the hydrogen separation rate into the cathode. (B) Carbon species balance and methane flow rate. (C) Applied current and measured potential in the MEA. (D) Carbon oxide generation rates and selectivity. (E) Hydrocarbon conversion and hydrogen recovery rates. (F) Anodic bubbler and internal PMR unit temperatures.

58.0 sccm for a maximum hydrogen recovery of 83.5%. At the initial reaction temperature, prior to electrochemical separation, the average steady-state methane conversion was 72.1%. The maximum conversion of methane during electrochemical separation at 9.00 A of electric current was 99.5%. A carbon oxide selectivity shift was also observed at the maximum hydrogen separation rate as the removal of SMR and WGS products pushed the equilibria of the reactions towards enhanced production of carbon dioxide. The ratio of carbon dioxide and carbon monoxide increased from 0.432 to 2.00 as a result. Joule-heating induced by the electrochemical separation of hydrogen increased the reactor temperature to a maximum of 822 °C, meaning 9.00 A of current supplied an additional 84.2 °C of internal heat to the PMR anode chamber. Throughout the dynamic experiment, the average membrane resistance was 0.380  $\Omega$ . With the exception of two brief resistance spikes at 190 min and 230 min, the electronic circuit demonstrated overall performance stability.

# 6.3. Relative gain array results

Fig. 11 provides an analysis on the independence of the proposed control loops using a steady-state RGA analytical tool. The operating ranges for manipulated variables were 0.00 to 9.00 A of MEA electric current, 10.0 to 40.0 sccm of inlet methane, and 104 to 131 °C bubbler temperature setpoints. To reduce the order of the gain matrix results from three to two dimensions, bubbler temperature setpoint constants of 120 °C and 125 °C were chosen since the initial T<sub>sp</sub> value was 120 °C and S/C ratios produced from T<sub>sp</sub> values greater than 125 °C would exceed 3.95 at the maximum methane inlet flow rate. For all combinations of operating conditions, the pressure of the lumped-parameter CSTR model was set to 3.15 bar and the catalyst weight parameter was set to 13.0 mg. At both  $T_{sp}$  values (Fig. 11), the normalized  $\lambda_{11}$ value is equal to 1.00 for all combinations of steady-state operating conditions, indicating the independence of Controller 1 on the control actions of the second and third PI controllers. In other words, the MEA electric current input variable is appropriately paired with the hydrogen separation rate output variable, and the first PI controller can

manipulate the MEA electric current without interacting with the other control loops in the control architecture. The RGA results for  $\lambda_{22}$  and  $\lambda_{33}$  reveal operating conditions in which the second and third PI controllers have well-paired inputs and outputs. However, there are also regions of operation where these two controllers may interact, potentially creating undesired or opposing effects on the target variables, which could undermine control objectives. The presence of coupling in the RGA does not mean single-loop PI control cannot be used, but rather indicates that single-loop PI control may not be as effective as a multivariable predictive control.

At the initial state of the process when  $T_{sp}$  is approximately 120 °C, the second and third PI control loops have  $\lambda_{22}$  and  $\lambda_{33}$  values at or close to 1.00 throughout the operational domain, indicating that the total hydrogen production rate and S/C ratio are only affected by the respective manipulated variables for each of the controllers. The effectiveness of the control architecture remains up until the electric current for hydrogen separation exceeds 4.00 A. Within the 15.0 to 20.0 sccm range for the methane feed flow rate, membrane currents exceeding 4.00 amps produce  $\lambda_{22}$  and  $\lambda_{33}$  values that range from –2.00 to 0.00. Ineffective or inverse control actions by Controller 2 or Controller 3 may arise in response to manipulation of the feed methane flow rate and  $T_{sp}$  in this operating regime.

The RGA results in Fig. 11B provide additional predictions of the MIMO architecture at membrane currents from 4.00 to 9.00 A and methane feed flow rates from 20.0 to 25.0 sccm at a  $T_{sp}$  equal to 125 °C. In this range, all three control loops have  $\lambda$  values from 1.00 to 2.00. The implication of the diagonal RGA values in these operating conditions is that all manipulated variables are directly correlated with the associated output variables. At methane feed flow rates ranging from 20.0–22.0 sccm, there are stronger than expected interactions for the Controller 2 and Controller 3 input–output pairings, but the PI control loop designs are still considered effective since the  $\lambda_{22}$  and  $\lambda_{33}$  values are above 1.00. Not only do we limit our operational domain as a result of this RGA analysis, we also test the operation experimentally to confirm that the coupling of these input–output variables does not inhibit the effectiveness of Controller 2 or Controller 3 in reaching the respective target setpoints. Note, control system stability is not directly



**Fig. 11.** MIMO RGA results at (A)  $T_{sp} = 120$  °C and (B)  $T_{sp} = 125$  °C. For  $\lambda_{ij}$  values below 0.00, red is used to indicate the potential for ineffective control actions in the specific operational domains. Light gray regions indicate non-feasible operating conditions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

determined by steady-state RGA analyses, and the subsequent control experiments were used to establish both the stability and effectiveness of the proposed control design for the PMR system.

#### 6.4. Multi-input multi-output setpoint tracking

The first set of PMR control experiments established the stability of the control architecture during transient operational states and at the desired target variable setpoints. A total hydrogen production setpoint of 150 sccm was chosen for Controller 2, and all three PI controllers were initiated at 107 min, after the system had achieved near-steadystate thermodynamic conditions. The continuous change in the hydrogen separation setpoint for Controller 1 due to the decisions made by the automatic setpoint generator suggests the experimental ratio of carbon dioxide to carbon monoxide was larger than 3.00:10.0 during setpoint tracking. This proposition is substantiated by the carbon oxide selectivity data provided in Fig. 12. Overall electronic stability, in addition to controller stability, was observed in Controller 1, with only one instance of a resistance spike to 0.404  $\Omega$  during initial control actions to increase the rate of hydrogen separation. Once the desired separation rate was achieved, the average final state of the MEA electric current was 6.85 A (or 0.451 A cm<sup>-2</sup>). After 159 min of control, the total hydrogen production rate in the PMR system reached the 150 sccm setpoint; thereafter, total hydrogen production rates remained within 4.60 sccm of the setpoint for Controller 2. To drive total hydrogen production to 150 sccm, the feed methane flow rate increased from 16.2 to 20.8 sccm. Over 99.0% conversion of methane was achieved at the desired hydrogen production rate setpoint, demonstrating increased kinetic reaction rates and movement of the thermodynamic equilibria of the SMR and WGS reactions. Due to increased rates of methane consumption and hydrogen recovery for positive setpoint tracking, the S/C ratio setpoint was elevated to 3.30 during control experiments to ensure adequate humidification of the ceramic anode materials. The coupling

of the back pressure regulator P controller actions with the cascading PI and PD controller actions of the third control loop produced oscillatory pressure effects in the anode and cathode reformer chambers. Still, the average S/C ratio was maintained at 3.30 by Controller 3, and anodic pressure oscillations were limited to  $\pm 0.245$  bar (Fig. 12). Therefore, the first experimental control scenario demonstrates the ability of the MIMO control scheme to maintain process stability in the presence of continuous or discrete disturbance phenomena.

A second control scenario was used to examine the feasibility of third control objective and perform multi-setpoint tracking of the second control loop. All of the aforementioned control approaches, digitalization efforts, and preliminary PMR control experiments advanced the system functionality to permit concurrent dynamic setpoint compensation of Controller 1 with multi-setpoint tracking of Controller 2. During positive and negative setpoint tracking, the second control loop effectively reached three total hydrogen setpoints in 114 min on average. The average absolute error, once the PMR system settled at a global hydrogen setpoint was 2.38 sccm. Methane feed flow rates ranged from 16.2 to 25.7 sccm throughout setpoint tracking, illustrating a synergy between the first and second control loops in achieving elevated hydrogen production rates above 100 sccm. A setpoint step change from 165 to 125 sccm, for the second control loop, demonstrated controller stability during considerable changes in the system state. Optimized  $K_c$ and  $\tau_I$  parameters allowed for positive and negative setpoint tracking, given the internal reactor temperature rate of change was limited to less than 5.00 °C during the global hydrogen flow rate ramps to 150 sccm and 125 sccm. However, there were two instances when this control objective was not achieved, which occurred at 350 min during a series of voltage spike across the membrane circuit. The voltage spikes occurred at the 165 sccm global hydrogen setpoint as the electric current approached the 10.0 A operating limit and resulted in an instantaneous  $0.150 \ \Omega$  jump in the membrane resistance that was likely due to a local decrease in water vapor partial pressures. Overall methane conversion



Fig. 12. MIMO controller stability results for a total  $H_2$  setpoint of 150 sccm ( $T_0 = 737$  °C |  $I_0 = 0.00$  A |  $q_{CH_1,0} = 16.2$  sccm |  $T_{sp,0} = 120$  °C). The average absolute uncertainty (AAU) for Controller 1 is an average of flow meter uncertainties throughout the control experiment (Alicat mass flow meter absolute uncertainty was  $\pm 0.6\%$  of flow reading).

remained above 85.4% for the extent of active controller regulation during the second control scenario.

At the maximum total hydrogen production rate, when the methane feed flow rate was 26.9 sccm, conversion continued to exceed 98.1%, once again demonstrating the forward progression of reaction equilibria at enhanced hydrogen separation rates. The hydrogen recovery and carbon oxide selectivity aligned with previous observations as well. The average hydrogen recovery ratio was 49.3%, and the mean carbon dioxide to carbon monoxide selectivity was 1.03. Controller performance resembled previous steady-state and single-setpoint tracking experiments during highly nonlinear, transient phases of control. PI Controller 3 enacted stable control actions during the steep ramp down of the feed methane flow rate at 400 min, quickly returning the S/C ratio to the setpoint by decreasing  $T_{sp}$  from 124 to 121 °C. This coupling of controller actions was captured in the RGA analysis that predicted controller interdependence for the second and third loops at 5.00 A electric currents at the observed  $T_{sp}$  and  $q_{CH_4}$  conditions. Still, the control system maintained stability, and two of the three control objectives were achieved. There were only two instances of control actions that violated the first control objective: a temperature rate of change of 8.03 °C min<sup>-1</sup> and -6.83 °C min<sup>-1</sup> during multisetpoint tracking. It is noted, however, that the violations occurred in only two instances over 460 min of adaptive MIMO control and had no observable impact on catalyst performance or the robustness of the control architecture.

#### 7. On autonomous data generation for PMR scale-up research

The superior input–output variable pairings for this multi-input multi-output control system at the selected operating conditions are: manipulation of the MEA electric current to control the hydrogen separation rate, modulation of the methane feed flow rate to control the total hydrogen production rate, and adjustment of the bubbler temperature setpoint to control the S/C ratio at the inlet stage of the PMR system. Evidence for the controlled variable pairings exists in the independence and stability of controller actions during multi-setpoint hydrogen control scenarios (Fig. 12). Thus, dynamic compensation may be used to automatically adjust the hydrogen in the reforming system over time (Fig. 13). Additionally, PI control effectively transitions the hydrogen production process between the desired process setpoints. Each controller in the MIMO scheme can be tuned to protect reformer metals and the material integrity of the catalyst by maintaining an S/C ratio above 3.00 during high rates of hydrogen separation at elevated electric currents. The lack of explicit constraints on the Controller 1 input, however, still allows for instances of Joule-heated temperature fluctuations, and model predictive control for Controller 1 is recommended in future works.

Steady-state experiments at increased reformer pressures, in the absence of proton migration through the BZCY membrane, show different catalytic weight parameters when compared to 1.00 bar anodic effluent compositions. It is possible that an irreversible change in catalyst activity occurred between experiments or that sensor error shifted-results. It is equally likely that Xu and Froment kinetics in the lumped-parameter model do not accurately capture surface reaction dynamics, since (Hsu et al., 2024) also reports a plant-model mismatch for model predictions at different reforming pressures. Systematic kinetic studies using lab-scale PMR units can improve process simulations by providing preexponential factors and apparent activation energies that account for the thin-film morphology of the catalytic layer. Kinetic data based on catalytically active surface areas need to be extracted and used to model and size these systems instead of the kinetic data based on the packedbed catalyst weight of the Xu and Froment kinetic model (Mbodji et al., 2012).

Safe and effective automation also allows for transient data generation to document time-variant kinetics and energy dynamics at the watt-scale. By employing this multivariable control architecture within RGA-affirmed operational regimes, the catalyst, electrode, and electrolyte materials are preserved to minimize maintenance times and reduce capital and operational costs. Like other experimental control systems (Cifuentes et al., 2023; Andreasen et al., 2013; Lin et al., 2006), we demonstrate the effectiveness and controllability of a hydrogen generation system using straightforward control algorithms within cascading loops for control of a nonlinear chemical processing system. The ability to automate the system, adapt hydrogen separation setpoints to improve electrochemical longevity, and as a result generate hundreds of hours of data on a single membrane, allows for the development of extensive thermo-electrochemical datasets that may be used to develop generalized multi-physics models to capture and predict transport and reaction kinetics for future kilowatt-scale PMR systems.

Sensor precision and reliability are seen as primary bottlenecks to advanced automation procedures using model predictive control, and any improvements to hydrogen uncertainties will greatly improve the reliability of PMR control systems over time. Online hydrogen



Fig. 13. MIMO closed-loop results for  $\pm$  setpoint tracking sequence:  $q_{H_2,tot}$  setpoint [150, 165, 125 sccm] (T<sub>0</sub> = 737 °C | I<sub>0</sub> = 0.00 A |  $q_{CH_4,0}$  = 16.2 sccm |  $T_{sp,0}$  = 120 °C). The average absolute uncertainty (AAU) for Controller 1 is an average of flow meter uncertainties throughout the control experiment (Alicat mass flow meter absolute uncertainty was  $\pm 0.6\%$  of flow reading).

measurement uncertainties in Cifuentes et al. (2023) were the same order of magnitude as the Controller 2 uncertainties ( $\pm$ 5.00–15.0 sccm). Further, real-time economic optimization of Controller 1 via model predictive control is likely to improve energy efficiencies once measurement uncertainties are minimized and a similar approach will be pursued in future work.

#### 8. Conclusions

The automation of a protonic membrane methane reforming system through a feedback control framework has been investigated for purified hydrogen production. Starting with a qualitative and physical examination of the control degrees of freedom of the PMR units, three manipulated variables were chosen as the control architecture inputs: the MEA electric current, methane feed flow rate, and S/C ratio. The combined impact of each manipulated variable on target process variables was modeled in Cui et al. (2024a) and was affirmed in preliminary PMR experiments. These diagnostic trials allowed PMR system users to define the operational domain for the manipulated control parameters. Derivation of a three-dimensional steady-state RGA then followed; specifically, all three control outputs were correlated with steady-state inputs in the RGA, which elucidated the points of operation that were least susceptible to controller interactions. By way of a nonlinear state estimator, the RGA considers the nonlinearity of the system, albeit for the nonlinear relationships between steady-state inputs and outputs.

Most importantly, we have demonstrated the multi-input multioutput controllability of a protonic membrane reformer in highly transient modes of operation over time. Equally noteworthy is the use of automation to couple and adapt the hydrogen separation rate to the state of the overall hydrogen production rate. With at least two control degrees of freedom remaining, additional control systems could be implemented to directly regulate reactor pressure and temperature to further optimize the operation of the process. This work, therefore, establishes the feasibility of multiple feedback loops with operational layers for automating and operating watt-scale PMR processes.

#### CRediT authorship contribution statement

Dominic Peters: Writing – original draft, Methodology, Investigation, Conceptualization. Xiaodong Cui: Writing – original draft, Methodology, Investigation, Conceptualization. Yifei Wang: Writing – original draft, Methodology, Investigation, Conceptualization. Christopher G. Donahue: Writing – original draft, Investigation. Jake Stanley: Investigation. Carlos G. Morales-Guio: Writing – original draft, Supervision, Funding acquisition, Conceptualization. Panagiotis D. Christofides: Writing – original draft, Supervision, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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