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Dynamic and steady state analysis of a power to methane system using a commercial solid oxide cell (SOC) electrochemical reactor

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Abstract

Higher penetration of renewable energy sources in the energy mix and increasing pressure to decarbonize society introduces new challenges. Energy storage and grid stabilization systems are necessary to address the intermittent nature of renewable energy sources (wind, solar etc.). Apart from the aforementioned challenges, moving towards a decarbonized economy, where electrical energy becomes the prime mover, new pathways to produce valuable and important chemicals (hydrocarbons etc.) should be established. Storing electricity in form of chemical energy is advantageous due to its long storage duration and its flexibility in use [1]. Methane is an important energy carrier and also an important raw material for various other process industries. Hence, converting renewable electricity to synthetic natural gas can address the issue of renewable energy storage and provide an alternate route for chemical energy required by process industries.

In this paper, a Power to Methane energy storage system based on the experimental study of a commercially available 10 layer SOC reactor is presented. Thermal management of the electrolysis process is addressed by considering different possibilities for heat integration. Pressurized operation of the system is considered to study the effect of internal methanation within the SOC reactor on the system performance. For the proposed system an electric to chemical energy conversion efficiency of 91 % is feasible under nominal steady state operation conditions. The effect of heat loss from SOC the reactor on the system performance is considered.

A dynamic study of the system is performed to study the impact of transient behavior on system performance and methane production. Additionally, strategies for transient operation are proposed to prevent hot spots, cold spots or sharp temporal and spatial temperature gradients in the SOC reactor that lead to eventual failure of the system are presented. For the above analysis an experimentally validated 1-D model of a reversible SOC reactor is used to study the temperature distribution in the SOC reactor during system operation

Introduction

Electricity storage is critical for a future energy system largely powered by renewable energy sources due to time varying supply and demand. Power to chemicals, where the chemicals can be gas or liquid, offers an interesting opportunity for large scale storage of renewable electricity [2]-[3]. Moreover, in moving towards to electricity driven society, alternate routes for chemical synthesis should be established. In this regard, storing electricity in the form of methane can be advantageous. Methane is a high value of chemical which has wider use in process industry and energy industry. Additionally, the existing natural gas grid can be used to the stored the produced methane thereby avoiding complex and expense gas storage systems. High temperature electrolysis using Solid Oxide Cell (SOC) electrochemical reactor systems can certainly address the above requirements. Due to high operation temperature of solid oxide electrolysis cell (SOEC) process, it is more efficient compared to low temperature electrochemical reactors [4]. Due to the oxygen ion conduction, co-electrolysis (electrolysis of water and carbon dioxide) can be performed to produce syngas which can then be used in appropriate downstream process to produce methane or other hydrocarbons. Under appropriate conditions, some amount of methane can also be generated within the SOC reactor [5]-[6]

Process system engineering of an SOEC system coupled to downstream process should take into different operation points that might be experienced by the system due to varying electricity input. This affects the operation of the SOC, downstream process, thermal management and ultimately the system performance. Depending on the end use of the methane produced, the quality and quantity of methane production at different operation times should be considered. These top level requirements presents further challenges on the process system engineering of a pressurized SOEC system coupled to a downstream methanation process.

In this paper, process system study of a pressurized SOEC system coupled to a downstream methanation process based on a commercially available SOC reactor is developed. The process system analysis considers the effect of different operation points on the system performance and methane production. Design option is presented to address these challenges. Dynamic analysis is performed to understand the impact of operation change and transition on the SOC reactor and system performance.

1. Scientific Approach

A process system layout for a power to methane system was developed based on an experimental analysis of a commercially available SOC reactor under pressurized conditions [7]-[8]. A black box and one dimensional SOC reactor model was developed for the process system study. The black box model was utilized for the system modeling and the 1-D SOC reactor model was check the temperature profile within the SOC reactor, ensure safe operation of SOC reactor by checking for critical operation conditions and to obtain the effective area specific resistance and temperature required as inputs for the black box model used in process system model.

A downstream methanation process model was developed based on the literature analysis of different methanation process. The literature survey was limited to existing methanation processes that are currently used in the industry. Based on the study, a 4 stage

intercooled methanation process was selected based on the commercial Haldor Topsoe TREMP™ process [9],[10].

The process system design should account for the boundary conditions for the SOC, methantion process, product gas composition at the design operation point and various off design operation points. For the SOC reactor, the temperature gradient within the SOC has to be controlled and maintained in order to keep the SOC in relatively stable operation environment. Sharp changes in spatial and temporal gradients should be minimized. This is constraint is critical since the SOC process can move between endothermic, thermoneutral and exothermic operation at different off design operation points. Finally, reactant conversion in the SOC reactor should be controlled such that carbon deposition doesn't occur within the SOC reactor and also outlet gas has sufficient H/C/O ratio to produce sufficient methane production in the downstream process.

For the downstream process, the conversion ratios in the methanation system should be monitored such that the product gas composition doesn't vary too much from the design condition. Moreover, the thermal integration between downstream methanation process, steam generation and process heating should also be monitored.

To account for all the different requirements at different operation points, steady state process system analysis was performed at design points and various off design points. From the steady state analysis, the key process system parameters, mass flow rates of steam-carbon dioxide mixture and air were determined such that the boundary conditions and requirements were met. The steady state results at different operation points are used as a reference for the development of the control strategy for transient operation.

2. Experiments/Calculations/Simulations

The process flow diagram of the power to methane system is described in Figure 1. Two design options are considered to be able to operate at off design conditions. In Figure 1, opportunities for heat integration in the form of solar thermal heat or process heat from other industries are indicated by dotted red arrows. The steam generation is coupled to the methanation system. The solid lines indicate the process flow at nominal design operation point. The two design option for off design conditions are shown in dashed lines and dash-dot-dot-dash lines. . Pressurized SOC and system operation is considered. The operation pressure of the system is fixed at 25 bar. The water and carbon dioxide flow rates supplied to the system are closely controlled in order to maintain an H/C ratio of 6-7 which is required for sufficient methane formation in the methanation process [10]. The SOC reactor conversion ratio (χ) is controlled such that the syngas from co-electrolysis has O/C ratio of 2 (minimum) to avoid carbon deposition. The conversion ratio is limited in the range of 78 % to 88 %. Pressurized air is supplied to the SOC reactor as sweep gas to flush out the oxygen produced during electrolysis. It also acts as heat transfer process to supply the SOC reactor with when operating in the endothermic mode or to remove heat from SOC reactor when it moves to exothermic operation mode. Air supply and air side process flows remain the same at all operation points. Mass flow rate of air is controlled to maintain the required thermal balance in the SOC reactor. A part of the air outlet from SOC is recycled and mixed with the inlet air. The recycle ratio is controlled such that the final air mixture temperature is close to the required inlet temperature. The recycle ratio is limit to 90 %. The SOC inlet temperatures for both air and CO_2 - H_2O mixture is fixed at 785 °C. The heat exchanger network (HEN) for the thermal management system (heat

recovery and steam generation) is designed such that it can operate within a bandwidth of 30-40 % above and below the nominal design point.

Nominal design operation point

At the nominal design operation condition, water from the tank is supplied to the steam generator which is thermal coupled to the methanation unit. CO_2 from the tank is preheated and mixed with the steam. The final mixture is preheated in the heat recovery unit and if required heat from external source such as solar is supplied to bring the reactants to the inlet temperature of 785 °C. The product syngas from the SOC is reactor largely consists of CO, H_2, CH_4 (due to internal methanation in SOC reactor) and unutilized CO_2 and H_2O. The product stream is cooled to the required inlet temperature of the methanation unit which is fixed between 270 – 320 °C. The heat production from methanation process is fed to the steam generation unit. The product gas rich in methane is cooled and sent to water knock out unit. The final dry gas is sent to the final user. Based on the final usage (for gas grid, chemical industry etc.) further processing can be done to match the final requirements.

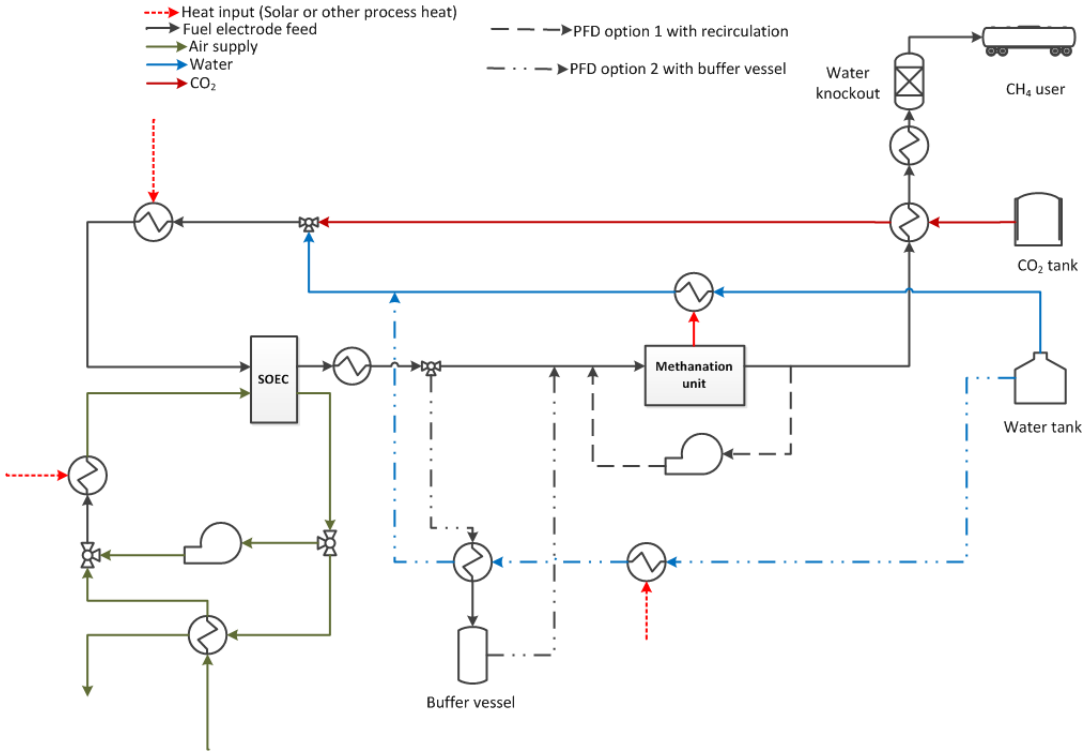

Figure 1: Process flow diagram of power to methane system using pressurized co-electrolysis and downstream methanation process. Steam generation is coupled to the methanation process. Design option (1) includes recirculation cycle in the downstream methanation process to handle off design condition. Design option (2) considers a decoupled downstream process using buffer volume vessel. Heat integration opportunities using solar thermal heat or process heat is shown using dotted red arrow.

Off design operation point

Design option 1: Product recirculation loop and varying conversion.

For the certain off design conditions, the process system can meet all the requirements of the system. One of the critical constraints is related to the heat recovery and steam generation that is coupled to the methanation unit. Secondly, when operating at SOC

capacity that is considerably lesser than the nominal capacity (40 % of nominal operation point), the mass flows in the systems are reduced considerably if conversion of the SOC reactants is maintained constant. This would result in the HEN unit coupled to the methanation system and heat recovery over designed for the mass flow leading to temperature crossing problems. On the other hand, when lowering the conversion in the SOC reactor, then composition of the final product gas is greatly affected. To address this issue a recirculation loop is suggested to recycle the product of methanation unit back to the inlet of the methanation unit. This would increase the conversion within the methanation unit and hence help in attaining product composition close to the nominal operation point.

Design option 2: Decoupled methanation with buffer volume and constant conversion
In the second design option, a decoupling of the methanation process from the SOC electrolysis process by means of a buffer storage volume is suggested. The SOC reactor is operated at constant conversion ratio at all operation points. The methanation unit is designed to operate around the nominal operation point at all times of operation.

At off design points above the nominal operation point, mass flow at the outlet of the SOC is higher than normal (since conversion ratio is kept constant in SOC), the output gas from the SOC is divided into two streams; one feeds the buffer volume and other feeds the methanation unit. The mass flow rate to the buffer volume is the difference between the mass flow at the outlet of SOC and mass flow to the methanation unit at nominal design condition. Part of the steam required for the SOC is generated in the steam generator linked to the methanation unit and corresponds on the mass flow rate of water corresponding to the nominal operation point. The excess water is converted in the auxiliary steam generator which takes the heat from the heat recovery unit coupled to the buffer stream. Additional heat if required is supplied to the auxiliary steam generation from external source such as the solar or an electric heater.

When the off design operation point is lower than the nominal condition, the flow rates to the system is lower than at nominal condition. Hence, a make-up syngas from the buffer volume is mixed with the gas from SOC outlet such that total mass is equal to nominal mass flow to the methanation unit.

By this arrangement, a constant conversion can be maintained in the SOC and also constant product gas composition and mass can be maintained. This also gives a greater flexibility in sizing of the two major units (co-electrolysis unit and the methanation unit). The SOC system can be sized for higher capacity than the methanation unit depending on the application and requirements.

3. Results

The process system was simulated in the nominal operation point and off design points for the two design options. The electricity input for the SOC at the nominal operation condition is treated as reference. The electricity input for SOC at off design operation points are normalized with respect to the electricity input at the nominal operation point. The heat input to the system is also normalized with respect to the electrical input to the SOC at the given operation point. The system performance for the both the design options are summarized in the Table 1 for the design options.

The power to methane conversion ratio is defined in equation 1, as the ratio of the electrical power input to the chemical energy of the product methane mixture (CH_4, some H_2 and CO_2) produced after the methanation process. Hence, for the design option 2, the power to methane conversion doesn't take into account the chemical energy of the syngas that is stored in the buffer tank at off design conditions.

Power to Methane % = Chemical energy of product (LHV) /Electrical power (1)

The heat input ratio (in %) is the ratio of external heat input to the total electrical power provided to the system.

Table 1: Performance overview of the system operation at nominal point and off design operation for design option 1 and design option 2

	Nominal operation point									
	Power to Methane ratio		Heat input ratio		Product composition at outlet after methanation in mol%					
					CH_4	H_2	CO_2			
100 %	91 %		8 %		92	6	2			
	Off design operation									
	Power to Methane ratio		Heat input ratio		Product composition at outlet after methanation in mol %					
	Design option 1	Design option 2	Design option 1	Design option 2	Design option 1			Design option 2		
					CH_4	H_2	CO_2	CH_4	H_2	CO_2
20 %	110 %	0	42 %	47 %	89	1	10	0	0	0
50 %	102 %	239 %	14 %	46 %	89	1	10	92	2	6
160 %	86 %	56 %	8 %	15 %	82	15	3	92	2	6
230 %	80 %	39 %	9 %	11 %	73	22	5	92	2	6

At nominal operation point, a power to methane ratio of 91 % is feasible. The electrolysis process is slightly exothermic resulting. Additional heat input is still required for process heating requirements. The product methane gas mixture has a molar composition of 92 % CH_4, 6 % of H_2 and 2 % CO_2 which can be further processed depending on the end use. If used for grid integration, nitrogen and sulfide should be mixed to meet the required gas density and Wobbe index or can be directly supplied to chemical industries. At off design conditions, the SOC moves between exothermic and endothermic operations.

For off design operation of 20 % and 50 % of nominal operation point, the SOC is endothermic. During endothermic operation mode, the power to methane ratio is greater than 100 % and heat input is also higher than at nominal condition. For design option 2, at 20 % of nominal operation point, the methanation unit is completely decoupled and is not operating. This is the cutoff point below which it is not possible to run the coupled system while still maintaining constant product gas composition and mass. At this condition all the syngas produced by SOC is sent to the buffer tank. Hence, there is no methane product production resulting in zero power to methane ratio based on the definition. At this point, since there is no methanation occurring all the heat required for steam generation must come from external source and hence resulting in a high heat ratio. Meanwhile at 50 % of the nominal operation for the design option 2, the power to methane ratio of 239 % is reached. An unrealistic high value is reached due to the definition of power to methane

ration. At this operation point, additional syngas mass flow from the buffer tank is sent to the methanation unit so that methanation system operates similar to nominal operation point to produce constant mass of the product with fixed composition.

At off design points above nominal operation point, the power to methane ratio decreases. The values are considerable lower for design option 2 when compared to design option 1. This is because, for design option 2, not all of the syngas produced by the SOC is sent to the methanation unit. Part of the syngas produced is sent to the buffer tank and remaining is sent to the methanation unit. The chemical energy of the syngas is not accounted in the definition of power to methane ratio.

The volume and composition of the product produced by the design option 2 is always constant as at nominal operation point whereas, for the design option 1 the composition varies drastically and also the volume varies. The final system design depends on the end user requirement. If constant production volume and composition is needed, design option 2 should be selected and the sizing of SOC and methanation unit can be varied to provide greater flexibility. If there is no constraint on the volume and composition of product, design option 1 can be selected where the methanation unit is always running. The system layout and operation has a strong impact on the control and transient operation. In either case, the SOC will move between exothermic and endothermic operation. Hence the controller should take care of the spatial and temporal gradient in the system. Control logic was developed for the thermal management of the SOC. Based on the steady state analysis; the electric power and mass flow of water-carbon dioxide mixture are controlled by feedforward block. The air mass flow to SOC is controlled based on the spatial and temporal thermal gradient constraint. Logic unit is established to check if it is exothermic or endothermic. For endothermic mode, the spatial thermal gradient is limited to -10 K and for exothermic the spatial thermal gradient is limited to 45 K. A brief operation of the control logic is shown in Figure 2. The power is varied from nominal operation to 160 % of nominal point in 1.5 minutes. It is brought back to nominal point and later reduced to 50 % of nominal operation. The system returns to nominal point. The controller responds accordingly and the thermal constraints are met at all the operation points and also during transition.

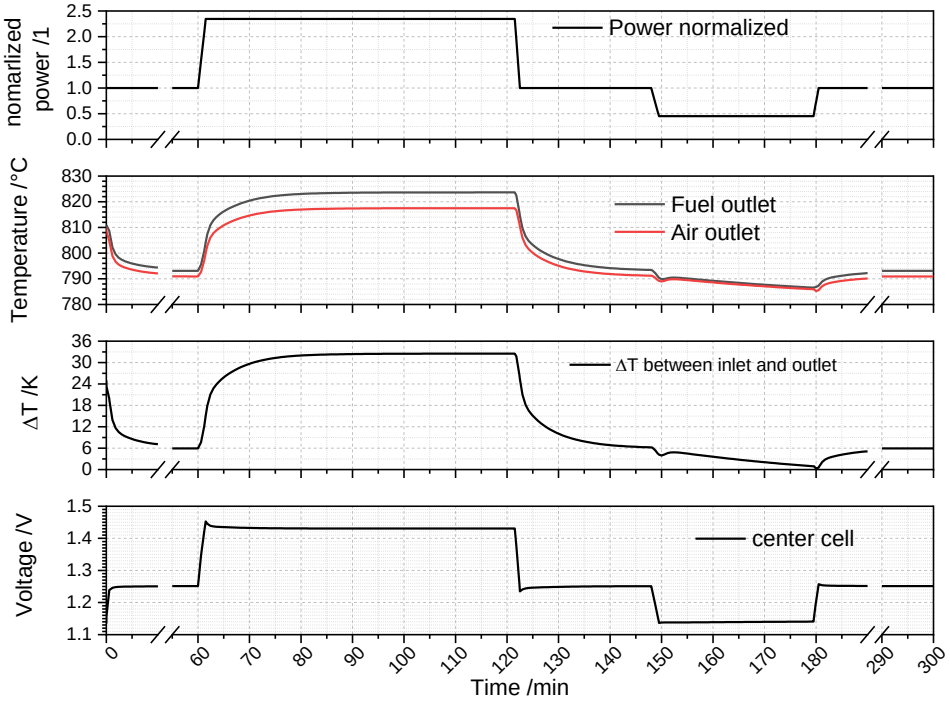

Figure 2: Transient behavior of SOC reactor and response to power change from nominal operation to 230 % nominal operation point and between nominal operation and 50 % of nominal operation point

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