Comprehensive Evaluation of Electrochemical Hydrogen Separator as Hydrogen Recovery Solution for Plasma Pyrolysis Assembly

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The previously tested State-of-the-Art (SOA) air revitalization architecture onboard the International Space Station recovers approximately 50% of the oxygen (O_2) from metabolic carbon dioxide (CO_2) via the Sabatier process. Maximum O_2 recovery is required to reduce resupply mass for long-duration manned missions. O_2 recovery is constrained by the limited availability of reactant hydrogen (H_2) from water (H_2O) electrolysis, and Sabatier-produced methane (CH_4) is vented as a waste product resulting in a continuous loss of reactant H_2. The Plasma Pyrolysis Assembly (PPA) has the potential to substantially increase O_2 recovery by post-processing the Sabatier-produced methane to recover H_2. The PPA decomposes CH_4 into predominately H_2 and acetylene (C_2H_2). A separation system is needed to purify the H_2 from the PPA stream before it is recycled back to the Sabatier reactor. Two sub-scale electrochemical H_2 separation systems, developed by Skyre, Incorporated, were delivered to NASA for evaluation. Complimentary of the previous submittal, ICES-2023-260, this paper reports a summation of Phase I and Phase II testing and evaluation of the C_2H_2 removal systems as well as lessons learned.

Nomenclature

2GPPA	=	*2nd Generation Plasma Pyrolysis Assembly*	*OGA*	=	*Oxygen Generation Assembly*
A	=	*Amperage*	*PCI*	=	*Precision Combustions Inc.*
AR	=	*Atmosphere Revitalization*	*PPA*	=	*Plasma Pyrolysis Assembly*
C_2H_2	=	*Acetylene*	*SBIR*	=	*Small Business Innovation Research*
C_2H_4	=	*Ethylene*	*SDU*	=	*Sabatier Development Unit*
C_2H_6	=	*Ethane*	*SmLPM*	=	*Standard milliliters per minute*
CDRA	=	*Carbon Dioxide Removal Assembly*	*SSMG*	=	*Solid State Microwave Generator*
CH_4	=	*Methane*	*V*	=	*Volts*
CM	=	*Crew Member*	*W*	=	*Watts*
CO	=	*Carbon Monoxide*	*WPA*	=	*Water Processing Assembly*
CO_2	=	*Carbon Dioxide*			
CRA	=	*Carbon Dioxide Reduction Assembly*			
GC	=	*Gas Chromatograph*			
H_2	=	*Hydrogen*			
H_2O	=	*Water*			
ISRU	=	*In-situ Resource Utilization*			
ISS	=	*International Space Station*			
MPPA	=	*Methane Post-Processor Assembly*			
MSFC	=	*Marshall Space Flight Center*			
N_2	=	*Nitrogen*			
NASA	=	*National Aeronautics Space Administration*			
O_2	=	*Oxygen*			

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I. Introduction

FOR long-duration human exploration missions, it is imperative that life support systems are reliable, self-sustaining, and automated to require minimal crew interaction. Atmosphere revitalization (AR) technology on the International Space Station (ISS) provides a breathable atmosphere and comfortable living environment for the crew. The current AR system includes temperature and humidity control, O_2 generation, trace contaminant control, CO_2 removal, and CO_2 chemical reduction. Humidity is comfortably maintained using condensing heat exchangers. O_2 is produced by electrolyzing H_2O using the O_2 Generation Assembly (OGA), which produces H_2 as a byproduct. Harmful volatile organic compounds and other trace contaminants are removed by the Trace Contaminant Control System. CO_2 is captured by the CO_2 Removal Assembly (CDRA) and returns air to the cabin. Prior to 2011, the CO_2 removed from ISS was vented overboard resulting in a loss of 92% of the required respiratory O_2. In 2009, the Sabatier CO_2 Reduction Assembly (CRA) was launched to the ISS and became fully operational mid-2011. As illustrated in Figure 1, CRA accepts CO_2 from the CDRA and H_2 from the OGA. Carbon dioxide from the CDRA is compressed and stored in tanks until the Sabatier is ready for operation. When the OGA is operational and CO_2 is available, the Sabatier system is activated to produce water and CH_4 via the Sabatier reaction shown in Equation 1.

Sabatier Reaction $$CO_2 + 4H_2 \leftrightarrow 2H_2O + CH_4 \quad (1)$$

The water produced is condensed and purified in the Water Processing Assembly (WPA) then recycled to the OGA. Methane, saturated with H_2O vapor, is vented to space as a waste product. This architecture recovers approximately 50% of the O_2 from metabolic CO_2 which is limited by the loss of H_2 in the form of vented methane and uncondensed water vapor in the methane stream. The CRA reduces the required water resupply from ~0.891 kg H_2O/crew member (CM)-day to ~0.459 kg H_2O/CM-day. However, the total water resupply necessary for a crew of four is ~670 kg H_2O/year for breathable O_2. NASA is targeting technologies that achieve 75-90% O_2 recovery from metabolic CO_2 for long duration missions beyond Low Earth Orbit[1]. One approach to achieve increased O_2 recovery, involves adding a Methane Post-Processor Assembly (MPPA) to the existing ISS AR architecture to recover H_2 from CRA-produced methane. NASA has been exploring the Plasma Pyrolysis Assembly (PPA) as a potential methane post-processor[2,3,4,5,6,7,8]. The PPA utilizes a magnetron to generate a H_2/CH_4 plasma targeting CRA methane conversion to H_2 and C_2H_2 as shown in Eq. 2. Secondary reactions with methane, shown in Eqs. 3-5, and reactions with residual H_2O vapor, shown in Eqs. 6-7, also occur resulting in an outlet stream mixture containing H_2, unreacted CH_4, product C_2H_2, and trace quantities of H_2O, carbon monoxide (CO), ethylene (C_2H_4), ethane (C_2H_6), and solid carbon (C).

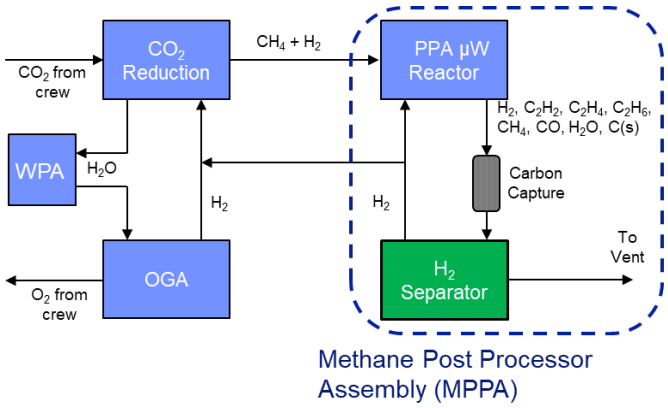


Figure 1: Proposed Flight Architecture Schematic for Plasma Pyrolysis Assembly (PPA) Methane Post-Processor Assembly Concept.

Targeted PPA Reaction	$2CH_4 \leftrightarrow 3H_2 + C_2H_2$	(2)
CH_4 Conversion to Ethane	$2CH_4 \leftrightarrow H_2 + C_2H_6$	(3)
CH_4 Conversion to Ethylene	$2CH_4 \leftrightarrow 2H_2 + C_2H_4$	(4)
CH_4 Conversion to Solid C	$CH_4 \leftrightarrow 2H_2 + C_{(S)}$	(5)
CO Production	$C_{(S)} + H_2O \leftrightarrow CO + H_2$	(6)
CO Production	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	(7)

When H_2 recovered from CH_4 by the PPA is recycled back to the CRA, operated at a H_2:CO_2 ratio of 4.25:1, a theoretical O_2 recovery of greater than 86% may be achieved (assuming a respiratory quotient of 0.92) from metabolic CO_2 which further reduces the necessary H_2O resupply to ~0.18 kg/CM-day (263 kg/yr). However, the hydrocarbon byproducts must be removed to prevent methane reformation and fouling of the CRA catalyst. In 2019, two sub-scale H_2 separation test articles, developed by Skyre, Incorporated (Skyre), were delivered to NASA for evaluation. These articles were tested by NASA at Marshall Space Flight Center (MSFC) in two progressing configuration Phases. This report addresses the results of the evaluations of these hydrogen separation test articles.

II. Hardware and Test Configuration

A. Hardware

The Skyre cell stacks are electrochemical H_2 separation cell stacks that provide a means of selectively isolating H_2 from a hydrocarbon gas mixture. In electrochemical separation, the H_2 molecule is electro-oxidized to protons and electrons at the anode, and the resulting protons are electro-reduced at the cathode, thus producing purified H_2. The electrochemical membrane, comprised of polybenzimidazole, should act as a proton acceptor to transport protons through the membrane where they will accumulate in the cathode. Prior to 2014, the basic technology was not directly applicable to the PPA due to the relatively significant concentration of CO in the product stream. At typical operating temperatures, the CO would preferentially adsorb on the catalytic electrodes in the cell and interfere with their ability to oxidize H_2. Through a Phase III Small Business Innovative Research (SBIR) contract (80NSSC18C0013), Skyre worked to identify and develop a membrane catalyst that maximizes H_2 pumping and minimizes C_2H_2 hydrogenation in a mixed gas stream containing CO and other hydrocarbons. During this effort, two three-cell electrochemical stacks (series and parallel flow configurations) were developed. "Series" implies that each cell stack receives its own gas and electrical inputs while "Parallel" implies that the gas and electrical inputs are split between each cell stack like a manifold. Illustrated in Figure 2, the gas stream from PPA enters the cell stack on the anode side of the membrane and the H_2 is separated through the polybenzimidazole membrane to the cathode side while other carbonous gases exit the anode outlet. All test configurations, outlined in this paper, were used to determine the baseline performance of the electrochemical cell stacks by incorporating system challenges separately to distinctly identify root causes the test article may have in an integrated test stand configuration.

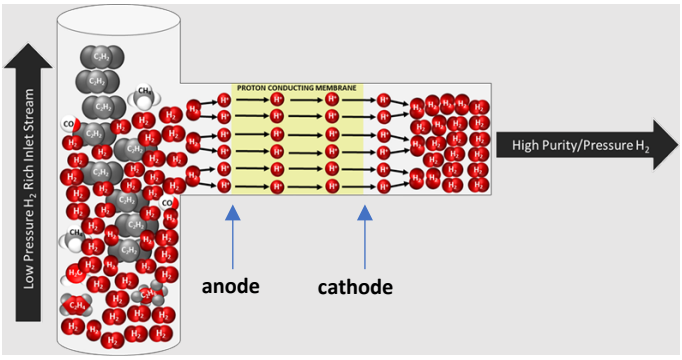


Figure 2: Diagram of Skyre Cell Stack

B. Test Configurations

1. Stand-Alone Operation Hydrogen Pumping Test

Both three-cell cell stack were tested in a stand-alone configuration to determine the baseline H_2 pumping performance. During operation, ultra-high purity H_2 was fed to the anode inlet of the cell stack. The gas enters the cell stack at the anode inlet, H_2 is separated and collected at the cathode outlet, and remaining gas exits the anode outlet as shown in Figure 3. Various tests were performed using dry H_2, and humidified H_2 induced by humidified N_2 with at least 4 hours of humidified pre-conditioning of the cell stacks. The humidified H_2 stream contained approximately 0.5 mol% H_2O vapor, induced by N_2 bubbled in DI water. The miniscule quantity of water vapor is anticipated in the PPA outlet stream during integrated Sabatier and PPA operations. Test results and further discussion is available in ICES-2023-260.

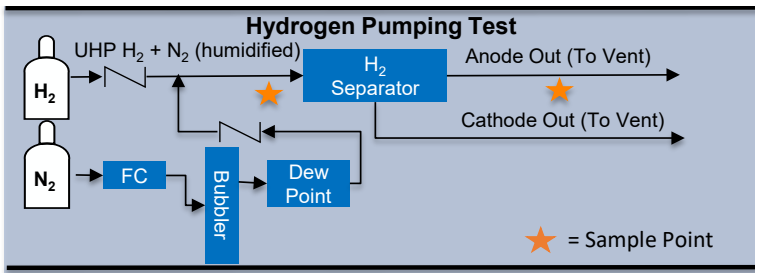


Figure 3: Stand-Alone Operation Hydrogen Pumping Test Configuration

2. Phase I Testing: PPA and H_2 Separation Operation

Both cell stacks were integrated with the 2nd Generation PPA (2GPPA) for initial evaluation as shown in Figure 4. In this configuration, the PPA was operated at a simulated 1-CM rate of CH_4 and an H_2:CH_4 ratio of 4:1 using compressed ultra-high purity H_2 and CH_4. The PPA reactor was maintained at ~52 torr with an applied microwave power of 450 W and a set frequency of 2450 MHz. This resulted in the PPA effluent containing H_2, C_2H_2, unreacted CH_4, C_2H_4, and C_2H_6. Operation in this manner prevented formation of CO and H_2O vapor. The resulting H_2 product was evaluated for purity and the process outlet stream was tested to identify vented composition using a micro-gas chromatograph (GC). Test results are available in ICES-2023-260.

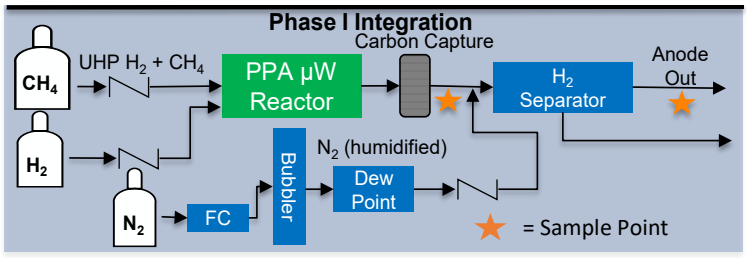


Figure 4: Phase I Integration Test Configuration

3. Phase II Testing: PCI Sabatier Development Unit (SDU) – PPA – H_2 Separation Operation

Both cell stacks were integrated with the Precision Combustions Inc (PCI) SDU and 2GPPA for integrated testing as shown in Figure 5. In this configuration, the PCI SDU was operated at a simulated 4-CM rate of CO_2 and H_2 and a H_2:CO_2 ratio of 4.5:1 using compressed ultra-high purity H_2 and CO_2. The SDU was maintained at 230°C and 14.5 psia while the 2GPPA was operated similarly to Phase I testing, accepting only 1-CM flowrate while remaining gas flow from the SDU was vented. This ensured that the electrochemical cell stacks would be tested at similar gas flow rates. Results from Phase II Testing are discussed in the following section of this paper.

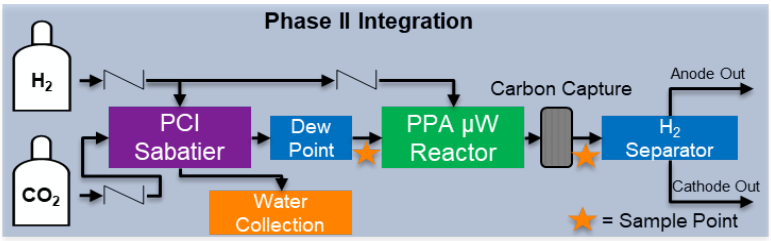


Figure 5: Phase II Integration Test Configuration

III. Results and Discussion

A. PCI Sabatier Standalone Test Results

Initial testing of the PCI Sabatier was performed to determine the operation conditions of the Sabatier reactor before integrating it in the test configuration shown in Figure 5. The PCI Sabatier converts CO_2 to CH_4, via the reaction in Eq 1, using a metallic monolithic catalyst structure. The exothermic reaction occurs at 425°C in the 1st chamber of the SDU reactor and 325°C in the 2nd chamber of the reactor. The exit gas stream is around 230°C which is condensed to ambient temperature before entering the 2GPPA Reactor. Test conditions are outlined in Table 1.

Table 1: PCI Sabatier Reactor Operating Parameters controlled by LabVIEW

PCI Sabatier Reactor Operating Parameters				
Output Resulting Variables	Reactor Pressure (psia)	Outlet Temperature Setpoint (°C)	CO_2 Flowrate (SLPM)	H_2 Flowrate (SLPM)
Dewpoint CO_2 Conversion %	14.0 – 14.5	230	1.0	4.5

Dewpoint of the Sabatier outlet stream was monitored to ensure the condenser was removing entrained water, produced in the reactor, from the outlet gas stream. Dewpoint proved to fluctuate with the temperature of the high bay facility and relative humidity would vary slightly between days. It was identified that the dewpoint varied between 7.7-9.0°C which indicates minimal water entrainment in the gas stream leaving the SDU. For a 2-hour steady-state operation period, the PCI Sabatier output a gas stream of 49% CH_4, 48% H_2, 2% unreacted CO_2, and ~1% water vapor.

B. SDU-PPA Integration Test Results compared to PPA Standalone Test Results

PPA Standalone testing should produce the most optimal reaction efficiency since the feed gases into PPA were ultra-high purity and would not contain unreacted feedstocks from prior unit operations. Excess water vapor and CO_2, components of PCI SDU outlet gas stream, contain oxygen which encouraged formation of CO from carbon via oxidation instead of C_2H_2 via hydrogenation of carbon. Table 2 provides the GC results of the outlet stream composition of the SDU-PPA outlet vs the PPA standalone test results previously discussed in ICES-2023-260.[9]

Table 2: Comparison of PPA outlet gas composition (%vol) results between Phase I and Phase II Tests

Gas Composition from Inficon GC	**PPA-H_2 Separator Testing (Phase I)**	**SDU-PPA-H_2 Separator Integrated Testing (Phase II)**
Acetylene (C_2H_2)	**8.2 – 8.4%**	**7.1%**
Ethylene (C_2H_4)	<0.1%	<0.1%
Ethane (C_2H_6)	<0.1%	<0.1%
Methane (CH_4)	0.6%	0.9%
Carbon Monoxide (CO)	N/A	2.7%
Carbon Dioxide (CO_2)	N/A	0.3%
Hydrogen (H_2)	**91%**	**88.6%**
Oxygen (O_2)	N/A	<0.05%
Nitrogen (N_2) – remnants from purge	N/A	0.2%

In accordance with the data in Table 2, reaction efficiency of CH_4 to C_2H_2 and H_2 for the SDU-PPA integration yielded a 95.5% reaction efficiency opposed to 96.9% reaction efficiency in PPA Standalone Testing[9].

$$\eta = \frac{x_i in - x_i out}{x_i in} \tag{8}$$

$$\eta_{PPA\ Standalone} = \frac{20.0 - 0.6}{20.0} = 96.9\% \tag{9}$$

$$\eta_{SDU-PPA\ Integration} = \frac{20.0 - 0.9}{20.0} * 100 = 95.5\% \tag{10}$$

C. Phase II Testing PCI SDU – PPA – H_2 Separation Results

Testing the cell stacks for hydrogen separation efficiency, derived from amperage produced from an applied voltage, required separate sets of trials performed at four specific temperatures where voltage and flowrate into the cell stack were varied. Separation efficiency of the cell stacks was calculated using Equation 11 where the moles of product H_2 in the cathode outlet and mol fraction of H_2 in the anode inlet were quantified using the GC data.

$$\eta_{Separation} = \left(\frac{n_{Cathode\ out\ H_2}}{n_{Anode\ in} * x_{H_2}}\right) * 100 \tag{11}$$

Humidified N_2 flow was held constant from test efforts forementioned in Section II B, and pressure was kept constant per the initial cell stack testing and evaluation supplied by Skyre. The test parameters for Phase II testing are displayed in Table 3 below.

Table 3: PCI Sabatier Reactor Operating Parameters for Phase II Testing

Skyre Cell Stack Operating Parameters					
Output Variables	Pressure (Torr)	Cell Stack Temperature (°C)	Voltage (V)	Water Content of Gas (% RH)	PPA Flowrate to Cell Stack (sccm)
Current (A) Separation Efficiency (%)	700	25	0.0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8	Varied depending on Sabatier Operation	250, 500, 1200, 1750
		100	0.0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8		250, 500, 1200, 1750
		170	0.0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8		250, 500, 1200, 1750
		180	0.0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8		250, 500, 1200, 1750

For comparison purposes, the results of Phase I testing are illustrated in Figures 6 and 7 below. These similar graphs can also be found in ICES-2023-260. To paraphrase the previous work, both parallel and series cell stacks from Skyre were capable of passing 75% of a ultra-high purity H_2 gas stream from the anode through the membrane into the cathode. This separation efficiency diminished to 35% at best once C_2H_2, CO, and CH_4 were introduced into the gas stream.

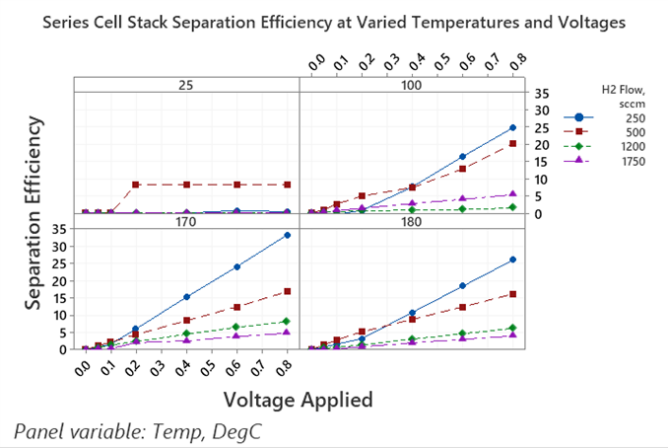


Figure 6: Phase I testing H_2 separation efficiency (series stack)

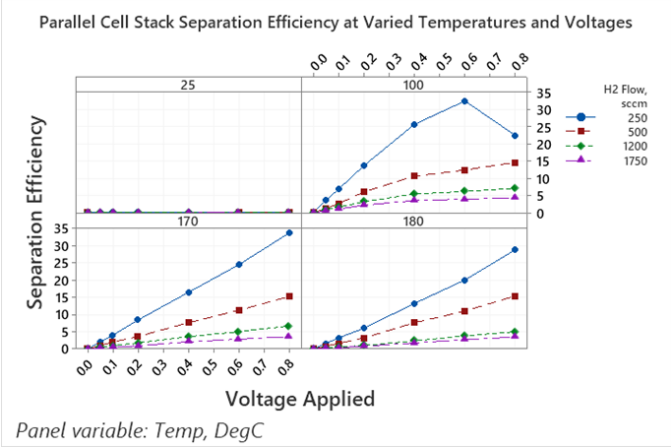


Figure 7: Phase I testing H_2 separation efficiency (parallel stack)

The results of Phase II testing are shown in Figures 8 and 9. In comparison with Figures 6 and 7, the hydrogen separation efficiency at 170°C and 180°C notably decreased from 35% efficiency to 15-20% efficiency with the addition of CO to the cell stack inlet gas per gas composition data in Table 2. The Skyre Cell Stacks were designed specifically to separate H_2 unhindered by CO, but this was disproven at multiple flowrate and temperature conditions within the test phases.

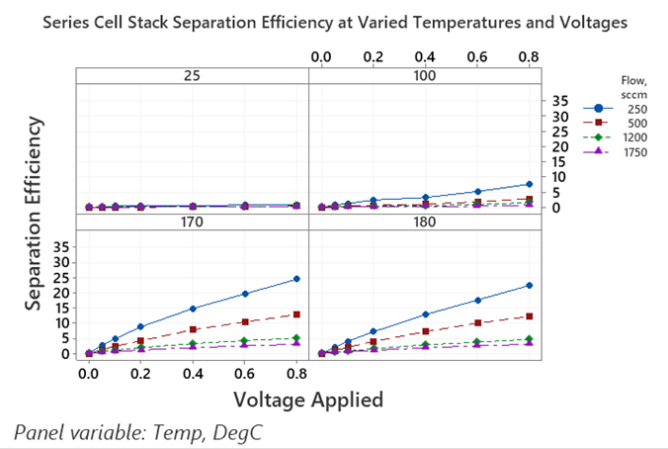


Figure 8: Phase II testing H_2 separation efficiency (series stack)

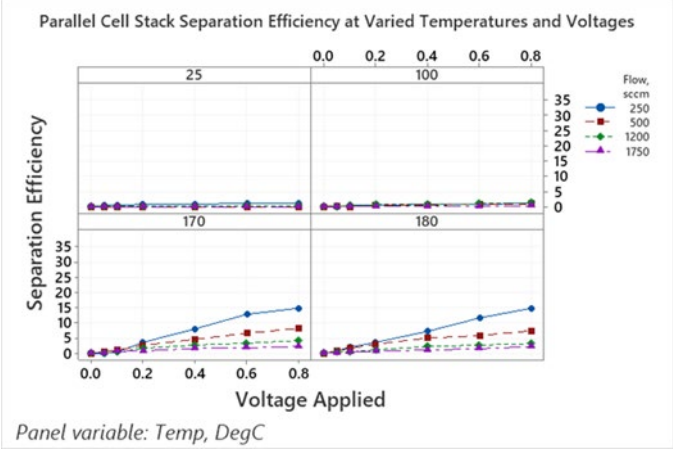


Figure 9: Phase II testing H_2 separation efficiency (parallel stack)

IV. Conclusions

The test results conclude that a carbon-based gaseous byproduct of the SDU-PPA configuration in both Phase II testing progressively decreased the reaction efficiency beyond the efficiency decrease noted in Phase I testing. Testing of the Skyre Cell Stacks was discontinued in summer, 2023 after failing to meet the performance baseline supplied by Skyre. Skyre notably achieved their deliverables per the SBIR Phase III endeavor for the project but further hardware troubleshooting, vendor consulting, and modifications was discontinued. NASA shifted focus to test stand development for an alternative hydrogen separation technology.

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