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# Investigation of the Electrochemical Looping Heat Pump in Heating Mode

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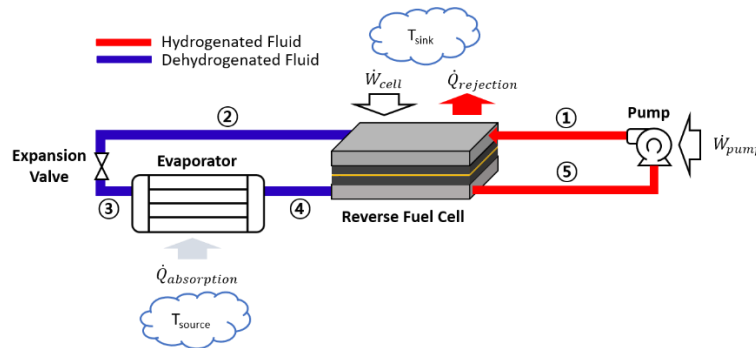
## ABSTRACT

The electrochemical looping heat pump (ELHP) is a novel thermodynamic cycle that incorporates a reverse fuel cell to achieve working fluid compression in the liquid state. Previous studies conducted by the authors demonstrated numerically the operation of the cycle in cooling mode and obtained performance improvements up to 20% with respect to conventional vapor compression cycle (VC) systems. In this paper, the cycle analysis has been extended to investigate heating mode operation. The primary focus of the study was the development of a working fluid screening process to determine suitable working fluid pairs while meeting low-GWP requirements. It was found that the developed screening process can be used to effectively control the cycle and the temperature of the fuel cell. Two working fluid pairs are identified, Isopropanol/Acetone and Ethanol/Acetaldehyde that yield COP improvements for heating compared to the best performing VC heat pump cycle (R290) of 21.8% and 13.5%, respectively. These working fluid pairs were selected from a wide number of hydrogenation/dehydrogenation reactions. It was discovered that these two working substance pairs are also the best performing in cooling mode. Finally, future research directions for this novel technology are identified.

## 1. INTRODUCTION

With the global population increasing, the down-phasing of fossil fuels and the growth of renewable electricity generation, heat pumping technologies have emerged as the primary candidates to meet future residential and commercial heating and cooling needs (IEA 2020, Calm and Didion 1998). Vapor compression (VC) cycles used for most HVAC, refrigeration, and growing water heating applications are approaching efficiency limits, and running out of potential environmentally friendly and safe refrigerants (U.S. DOE E3 Initiative, IPCC AR6). Therefore, there is renewed interest in non-VC technologies that can potentially have higher efficiencies and utilize natural or low-GWP refrigerants (Brown and Domanski 2014). The Electrochemical Looping Heat Pump (ELHP) is a novel thermodynamic heat pumping cycle first proposed by James et al. (2019) and illustrated in Figure 1. The novel features of this cycle include the use of: (1) a reversed fuel cell that performs a hydrogenation/dehydrogenation reaction, (2) a liquid pump in place of the vapor compressor, which reduces power input requirements (3) natural refrigerants for the electrochemical reactions. Previous thermodynamic analysis (Kim et al. 2020, Kim et al. 2021) has demonstrated that the Coefficient of Performance (COP), the ratio of heating or cooling output per electricity input, increases by 20% over conventional VC system in cooling mode for the same source and sink temperatures. However, there has not been any investigation in the literature of this cycle in heating mode yet. Due to the nature of the reactions in the cell and species transport ( $H^+$ ,  $e^-$ ), significant heat content is available even at very low temperatures while using natural working substances. Fundamentally, the ELHP aims to bridge the scientific fields of electrochemistry (batteries, catalysts, etc.) with thermal systems to harness specific advantages of electrochemistry; interfacial reactions without harmful bi-products, and producing phase change, for thermal applications.

The present study has investigated the performance (COP) of the cycle in heating mode and identified working substances that would allow for year-round operation. Additionally, a control scheme is provided that ensures phase change occurs across the cell. Lastly, key areas of future research are identified that would allow for the rapid growth of this technology.



**Figure 1:** Electrochemical looping heat pump (ELHP) cycle schematic (Adapted from James et al. 2019).

## 2. THERMODYNAMIC MODEL

### 2.1 Cycle Description

The concept at the essence of the ELHP is to utilize two different working substances, that have different saturation temperatures. The difference in saturation temperatures at a given pressure can allow for one substance to exist in a liquid state and the other in a gaseous state. The advantage to this is that compression of a liquid requires a significantly smaller power requirement than that of gas for a given mass flow rate. An electrochemical reaction is a controlled process that allows for the change of working substance and state to take place. The elements where electrochemical reactions occur can be categorized based on the type of species transfer.

**Table 1:** Typical Electrochemical Elements

Element	Species	Closed or Open System	Operational Temperature [°C]
Battery	Electrons ( $e^-$ )	Closed	21
Redox Flow Battery	Electrons ( $e^-$ ) and occasionally Hydrons ( $H^+$ )	Open or Closed	21
<b>Fuel Cells</b>			
Proton Exchange Membrane Fuel Cell	Electrons ( $e^-$ ) and Hydrons ( $H^+$ )	Open	60
Alkaline Fuel Cell	Electrons ( $e^-$ ) and Hydroxides ( $OH^-$ )	Open	100
Molten Carbonate Fuel Cell	Electrons ( $e^-$ ) and Carbonates ( $CO_3^{2-}$ )	Open	600
Solid Oxide Fuel Cell	Electrons ( $e^-$ ) and Oxides ( $O^{2-}$ )	Open	1,000

Table 1 reports the most common types of electrochemical systems as well as the species transfer that takes place. Batteries require charging/discharging and although they do produce and consume heat through entropy changes that occur during their oxidation and reduction reactions, they are not suited for continuous systems. Redox Flow Batteries (RFBs) on the other hand can be integrated into an open/looping system (see Gerlach and Newell 2006, Duan et al. 2021). However, the relevant reactions cannot produce a phase change as required in the cycle architecture of the ELHP (McKay et al. 2019). Therefore, a fuel cell is the primary candidate for this system. There are four main types of fuel cells as categorized by the species transferred through their membranes, Proton Exchange Membrane Fuel Cells (PEMFCs), Alkaline Fuel Cells (AFCs), Molten Carbonate Fuel Cells (MCFCs), and Solid Oxide Fuel Cells (SOFCs). Of these fuel cell types, only PEMFCs are suitable for the operational temperature of residential and commercial heat pumping and refrigeration applications. The others have the potential to be used in the same cycle architecture for high-temperature applications (industrial, space, etc.).

Having established PEMFCs as the only candidate, one might wonder how a power element (electrolyte in, power out) can be used for a heat pumping or refrigeration application. This is through reversing the operation of the system

whereupon, power is inputted to enable species transformation. These cells are referred to as *Reverse* or *Regenerative* in the electrochemical literature. The typical reactions used in the ELHP are those of the hydrogenation of acetone ( $C_3H_6O$ ) on the fuel cells cathode and the dehydrogenation of isopropanol ( $C_3H_8O$ ) on the anode.



where  $l$  and  $g$  indicate the phase of each substance. The challenge in the selection of a working substance pair lies in finding a natural substance pair that can: (1) electrochemically close the cycle loop through an exchange of  $n$  moles of  $H^+$  (2) undergo phase change at the given cell temperature  $T_{cell}$  (3) operate with a minimum power input requirement (high COP) (4) react with low-cost catalysts that also enable high reversibility and selectivity. The work presented in this publication is focused on criteria one through three.

## 2.2 Cycle Model

The thermodynamic cycle model is based on mass, species, and energy balance equations for each of the cycle's components shown in Figure 2. While more detailed explanations of the system and the set of equations are given in James et al. 2019 and James et al. 2016, the main equations used, alongside the key system constants are summarized in Table 3. The significance of all system variables is presented in the nomenclature.

**Table 2:** Equation set for the thermodynamic modeling of the components of the ELHP

Component	Equations	Assumptions
Reverse Fuel Cell	$w_{cell}^0 = -\Delta\bar{g} = - \sum_{i,prod} \nu_i \bar{g}_i - \sum_{j,react} \nu_j \bar{g}_j$ $g = h - Ts \text{ \& } h = h_f^0 + h(T)$ $h(T) = \int_{T^0}^T c_p dT \text{ \& } s = s_f^0 + s(T)$ $s(T) = \int_{T^0}^T \frac{c_p}{T} dT - R \ln\left(\frac{P}{P^0}\right)^n$ $V_{cell}^0 = \frac{-\Delta g}{n_e F} \text{ \& } n_e = 2n_{H_2}$ $V_{cell} = \frac{V_{cell}^0}{\eta_{cell}} \text{ \& } \dot{W}_{cell} = V_{cell} I$ $I = \dot{n}_{fluid} n_e F$	<ul style="list-style-type: none"> <li>• Ideal gas/compressed liquid reaction with varying heat capacity</li> <li>• Reaction to completion</li> <li>• Reversible with respect to the reactions</li> <li>• Selective (no bi-products).</li> <li>• Constant temperature <math>T_{cell}</math> through the cell</li> <li>• Losses are accounted for in <math>\eta_{cell}</math></li> </ul>
Expansion Valve	$h_{\textcircled{3}} = h_{\textcircled{2}}$	<ul style="list-style-type: none"> <li>• Isenthalpic</li> </ul>
Pump	$\dot{W}_{pump} = \frac{\dot{m}v(P_{high} - P_{low})}{\eta_{pump}}$	<ul style="list-style-type: none"> <li>• Negligible heating</li> <li>• Constant Viscosity</li> <li>• Losses account for in <math>\eta_{pump}</math></li> </ul>
Evaporator	$h_{evap} = h_{vap} - (h_{LiQ,\textcircled{2}} - h_{LiQ,\textcircled{3}})$ $h_{vap} = \frac{\ln\left(\frac{P_2}{P_1}\right)R}{\frac{1}{T_2} - \frac{1}{T_1}}$ $T_2 = T_{evap} + 0.5 \text{ \& } T_1 = T_{evap} - 0.5$ $P_2 = P_{sat,T_2} \text{ \& } P_1 = P_{sat,T_1}$	<ul style="list-style-type: none"> <li>• Superheat neglected</li> </ul>

It is noteworthy to mention some key modeling aspects and notations used. The subscripts  $i$  or  $j$  indicate a product or reactant species whereas the circled numbers indicate a state point. For example, state point 2 is represented as  $\textcircled{2}$ . The system is operating between a low and a high pressure. The low pressure is such that the dehydrogenated fluid is saturated at the evaporator temperature, and the high pressure is set so that it leaves the cell as a saturated liquid.

$$\begin{aligned} P_{low} &= P_{sat}(fluidB, T_{evap}) \\ P_{high} &= P_{sat}(fluidB, T_{cell}) \end{aligned} \quad (1)$$

In the above equation,  $fluidB$  is the dehydrogenated working fluid (for example acetone) and  $fluidA$  is the hydrogenated (isopropanol). The heat produced by the cell and the  $COP_H$  of the system are:

$$\dot{Q}_{cell} = \dot{n}_{fluid}\Delta H + \dot{W}_{cell} = \dot{Q}_H \quad (2)$$

$$COP_H = \frac{\dot{Q}_H}{\dot{W}_{cell}} \quad (3)$$

and finally, the evaporator and cell temperatures are found through pinch analysis.

$$\begin{aligned} T_{cell} &= T_{sink} + \Delta T_{pinch} \\ T_{evap} &= T_{source} - \Delta T_{pinch} \end{aligned} \quad (4)$$

In heating mode, the sink is the indoor environment and the source the ambient while the opposite is true for cooling. The indoor/sink temperature was selected as per the AHRI 210/240 H Standard (2017) (dry bulb) to be 21.1 °C (70 °F), whereas the outdoor temperature is varied to investigate the performance of the cycle. Similarly, in the cooling analysis presented in the latter sections,  $T_{indoor/source} = 21.1$  °C and  $T_{ambient/sink}$  are varied.

**Table 3:** System modeling parameters

Parameter	$\eta_{cell}$ [-]	$\Delta T_{pinch}$ [K]	$T_{ambient}$ [°C]	$T_{indoor}$ [°C] H or C	Superheat [°C]	Subcooling [°C]
Value	0.6	5	-30 to 20 (H) / 30 to 40 (C)	21.1	0	0

### 2.3 Saturation Model and Limiting Temperature

The analysis in this section involves varying  $T_{cell}$  freely (Eq. 4 represents a minimum constraint) to investigate the dynamics of the conversion process. The critical requirement in the ELHP is that the  $fluidB \rightarrow fluidA$  reaction produces a phase change from gas to liquid. This reaction occurs at the low system pressure (Eq. 1). The phase change requirement can be expressed as:

$$T_{cell} < T_{sat}(fluidA, P_{low}) \quad (5)$$

As the aim is to create an operational envelope for the cell temperature, we require an additional constraint that is given by the requirement to extract heat from the cell (2<sup>nd</sup> Law of Thermodynamics):

$$T_{cell} \geq T_{sink} + \Delta T_{pinch} \quad (6)$$

Equation 6 represents the requirement that heat is transferred from the cell indoors in heating operation or rejected to the ambient when cooling.  $\Delta T_{pinch}$  in this regard represents the temperature difference required for heat transfer to occur between the cell and the heat sink. Since the sink temperature is a piecewise function between cooling and heating, it can be expressed in the following form:

$$T_{sink} = \begin{cases} T_H = T_{indoor} & \therefore \text{Heating} \\ T_H = T_{ambient} & \therefore \text{Cooling} \end{cases} \quad (7)$$

Having created an upper bound for the cell temperature in heating and cooling, we can now define the region of operation. With respect to the refrigerants which are all natural (low GWP); unlike the industry standards HFCs, HFOs or HCs (R290), phase change and transport properties were not readily available. Thermodynamic libraries within available software, such as CoolProp, F-Chart EES and REFPROP only contain a small subset of the substances investigated (less than 10%). Therefore, the Antoine Equation was used. The fitting parameters were selected to be below the Normal Boiling Point (NBP) to ensure the accuracy of the non-linear fit and were obtained from NIST WebBook or fitted from experimental data (Bell et al. 2014, Afeefy et al. 2022).

$$\log_{10}(P_{sat}) = A - \frac{B}{C + T_{sat}} \quad \text{or} \quad T_{sat} = \frac{B}{A - \log_{10}(P_{sat})} - C \quad (8)$$

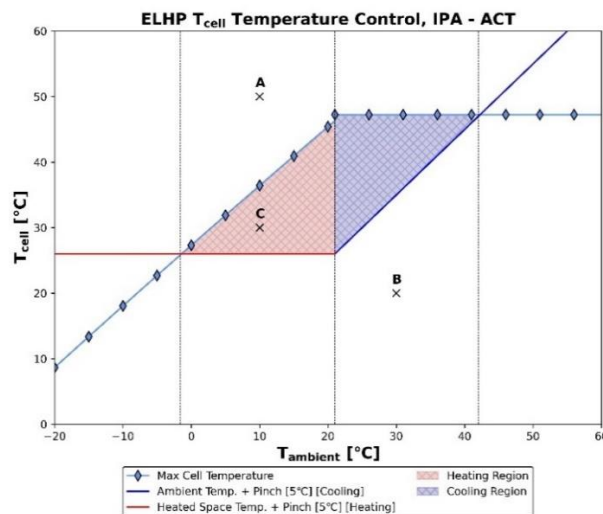
Of the substances presented in Figure 4, most of the Antoine equation parameters were obtained using the NIST WebBook (Afeefy et al. 2022). Of the missing substances, cyclopentene, 2-pentanone and 1,5 cyclooctadiene were obtained using the CRC Handbook of Chemistry and Physics. Lastly, hexafluoro-2-propanol and decalin parameters were fitted from the vapor pressure experimental data of Rochester and Symonds (1973) and McCullough et al. (1957) while the data for hydroxyacetone while missing from NIST were obtained directly from Petitjean et al. (2010).

### 3. WORKING SUBSTANCE SCREENING

#### 3.1 Cell Temperature Envelope

The operational envelope for the isopropanol (IPA) acetone (ACT) working pair is illustrated in Figure 2. The red highlighted region represents the range of cell and ambient temperatures where ELHP heating is possible, whereas the blue region is for feasible cooling operation. For heating, the lower bound is dictated by a minimum temperature difference necessary for heat transfer to the room ( $\Delta T_{pinch}$ ) and the upper bound is defined by saturation temperature associated with fluid A defined by Equation 5. The saturation temperature has a linear dependence on ambient temperature (Figure 2 blue line), since  $T_{sat,fluidA} - T_{sat,fluidB}$  is nearly constant at low pressures. For cooling, the lower bound is dictated by a minimum temperature difference for heat transfer to the ambient ( $\Delta T_{pinch}$ ) and the upper bound is the fluid A saturation temperature that is fixed because the indoor setpoint is constant. The vertical boundary between the heating and cooling regions is a room setpoint for cooling and heating. To further explain the physical significance of this plot, three example points were selected and are discussed below.

- (A)  $T_{cell} = 50\text{ °C}$  and  $T_{ambient} = 10\text{ °C}$ . This point is above the allowable cell temperature line. In this region, gaseous isopropanol is generated and therefore the cycle architecture is compromised. For a given design, this can be avoided by employing sufficient coolant flow rate for the cell temperature to be lowered to acceptable limits.
- (B)  $T_{cell} = 20\text{ °C}$  and  $T_{ambient} = 30\text{ °C}$ . This point is below the minimum value necessary to transfer heat from the cell to the ambient. However, since the cell is (1) exothermic and, (2) is initially at thermal equilibrium with its surroundings and located in an external housing, this condition is impossible to occur in cooling operation. This situation is primarily of concern in heating (for example  $T_{ambient} = T_{cell} = 0\text{ °C}$ ), when the reduced electrochemical kinetics (temperature dependent) might choke the cell's operation. In that case, it should initially be heated up to an optimal temperature after which the electrochemical reactions and flow of species can meet the heating load.
- (C)  $T_{cell} = 30\text{ °C}$  and  $T_{ambient} = 10\text{ °C}$ . This represents an appropriate heating mode operation where the gaseous acetone is converted to liquid isopropanol.



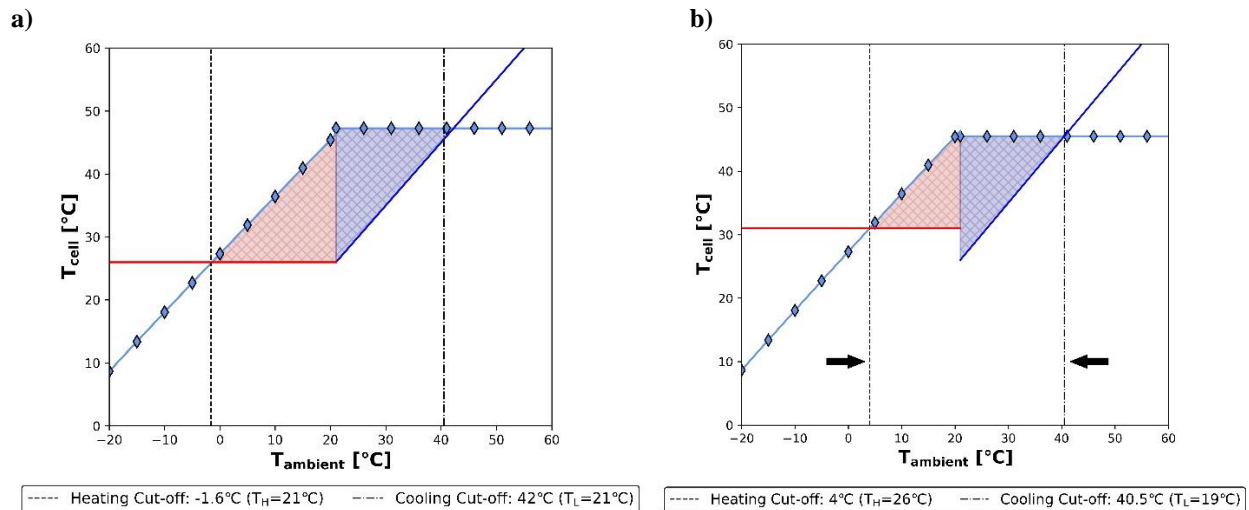
**Figure 2:** Control envelope for the IPA-ACT pair for an ambient temperature of -20 to 60 °C.

The vertical line located at -1.6 °C indicates the transition between heating mode and switch-off of the cycle since no feasible operation region exists above the required minimum cell temperature. Therefore, the lowest operational

ambient temperature for the IPA-ACT working pair is  $-1.6\text{ }^{\circ}\text{C}$  for the given heating setpoint and pinch. On the other side of the graph, in the cooling region, the vertical line at about  $42\text{ }^{\circ}\text{C}$  indicates a point where the system can no longer produce a cooling effect. This is because, again, as the ambient temperature increases, the system is no longer able to extract heat from the cell while maintaining a liquid to gas reaction at the cell's cathode. If no region of operation for a working fluid pair based on its saturation data exists, i.e., the maximum cell temperature is always below the required minimum, it can be eliminated.

### 3.2 Indoor Temperature Setpoint Effects

Changing the indoor temperature setpoints can either increase or decrease the allowable operating temperature range of the ELHP. For example, setting the indoor temperature to  $26\text{ }^{\circ}\text{C}$  in heating and  $19\text{ }^{\circ}\text{C}$  in cooling, results in updated shut-off temperatures of  $4\text{ }^{\circ}\text{C}$  and  $40.5\text{ }^{\circ}\text{C}$  for heating and cooling respectively. This also makes the cell temperature control requirement more stringent as shown in Figure 3.



**Figure 3:** Effect of indoor conditions on cycle limits a) original values (same as Figure 2) b) updating  $T_H = 26\text{ }^{\circ}\text{C}$  and  $T_L = 19\text{ }^{\circ}\text{C}$  for heating and cooling. The arrows indicate the cut-off temperature shift direction.

### 3.3 Reaction Pair Selection

The elimination procedure described in the previous section was applied to the working substance list presented in Table 4. A total of 30 reactions of the form  $A + nH^+ \leftrightarrow B$  were identified and investigated. Each of these reactions can occur in the temperature range suitable for heat pumping applications.

Although the criteria for selection have so far been thermodynamic, using safe (Low Toxicity and Flammability) substances is required. However, none of these substances have a refrigerant classification from ASHRAE Standard 34. To overcome this, the National Fire Protection Agency (NFPA) classification was used. As discussed in Section 4, since the cycle is not bidirectional, unlike conventional VC technology, since the fuel cell can only generate heat (exothermic component), we require that it operates in an outdoor unit with externally switching coolant lines (water-glycol mixture). Therefore, we expect the safety requirements to be a mixture of those for Ammonia ( $H \leq 3$ ) and Propane ( $F \leq 4$ ). Additional fluid restrictions involving other attributes (carcinogenicity for example) are made on a per case basis.

From Table 4, it is immediately apparent that the investigated substances have a significantly lower GWP, on average less than 25 (Low Classification), when compared with conventional refrigerants. Of the 15 candidate pairs, 8 were eliminated due to thermodynamic criteria (cannot operate in cooling or heating), 2 were eliminated due to other criteria (Furan has a very low flash point, Formaldehyde is highly cancerogenic) and 5 were found to be suitable for operation in the cycle.

**Table 4:** Detailed working fluid selection for the Electrochemical Looping Heat Pump.

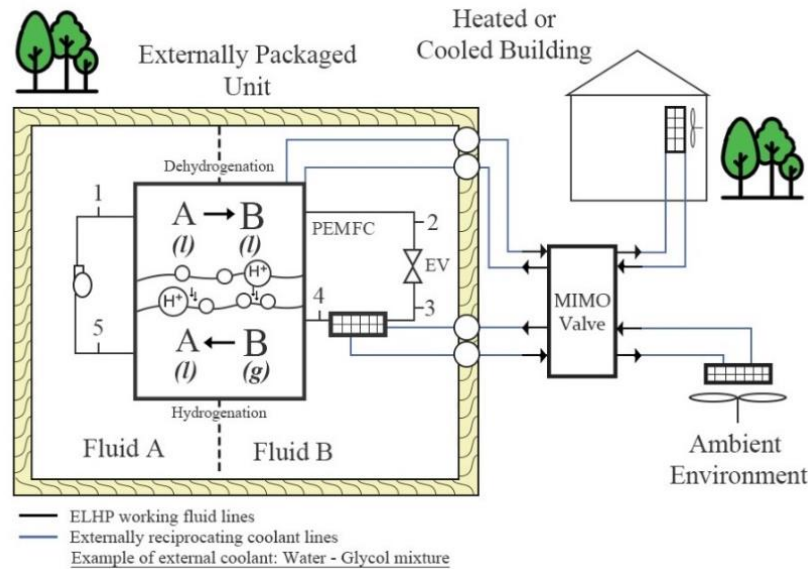
List of EWFs Pairs	Chemical Reactions	GWP FluidA/FluidB	NFPA Spec. FluidA/FluidB	Eliminated Y/N
Hexafluoro-2-propanol / Hexafluoroacetone	$(CF_3)_2CHOH \leftrightarrow (CF_3)_2CO + 2H^+ + 2e^-$	195 N/A (>100)	H:3 F:0 I:0 H:4 F:1 I:1	Y
Isopropanol/ Acetone	$C_3H_8O \leftrightarrow C_3H_6O + 2H^+ + 2e^-$	Low Low	H:2 F:3 I:0 H:1 F:3 I:0	N Most Promising Candidates
Tetralin/ Naphthalene	$C_{10}H_{12} \leftrightarrow C_{10}H_8 + 4H^+ + 4e^-$	Low Low	H:2 F:2 I:1 H:2 F:2 I:0	Y NBP of Naphthalene is 217 °C
Decalin/ Tetralin	$C_{10}H_{18} \leftrightarrow C_{10}H_{12} + 6H^+ + 6e^-$	Low Low	H:2 F:2 I:0 H:2 F:2 I:1	Y
Cyclopentane/ Cyclopentene	$C_5H_{10} \leftrightarrow C_5H_8 + 2H^+ + 2e^-$	Low Low	H:3 F:3 I:0 H:3 F:3 I:0	Y
Cyclooctane/ 1,5 Cyclooctadiene	$C_8H_{16} \leftrightarrow C_8H_{12} + 4H^+ + 4e^-$	Low Low	H:1 F:3 I:0 H:2 F:2 I:0	Y
Cyclohexane/ Benzene	$C_6H_{12} \leftrightarrow C_6H_6 + 6H^+ + 6e^-$	Low Low	H:2 F:3 I:0 H:2 F:3 I:0	Y
Methanol/ Formaldehyde	$CH_3OH \leftrightarrow CH_2O + 2H^+ + 2e^-$	Low Low	H:2 F:3 I:0 H:3 F:2 I:0	Y Formaldehyde is Cancerogenic
Ethanol/ Acetaldehyde	$C_2H_6O \leftrightarrow C_2H_4O + 2H^+ + 2e^-$	Low Low	H:3 F:3 I:0 H:3 F:2 I:0	N
Butanol/ Butanone	$C_4H_{10}O \leftrightarrow C_4H_8O + 2H^+ + 2e^-$	Low Low	H:1 F:3 I:0 H:2 F:2 I:0	N
2-Pentanol/ 2-Pentanone	$C_5H_{12}O \leftrightarrow C_5H_{10}O + 2H^+ + 2e^-$	Low Low	H:2 F:2 I:0 H:3 F:2 I:0	N
Propylene-glycol/ Hydroxyacetone	$C_3H_8O_2 \leftrightarrow C_3H_6O_2 + 2H^+ + 2e^-$	Low Low	H:2 F:1 I:1 H:1 F:2 I:1	N
1,2- dimethylcyclohexane/ o-xylene	$C_8H_{16} \leftrightarrow C_8H_{10} + 6H^+ + 6e^-$	Low Low	H:2 F:3 I:0 H:3 F:3 I:0	Y
Tetrahydrofuran/ Furan	$C_4H_8O \leftrightarrow C_4H_4O + 4H^+ + 4e^-$	Low Low	H:2 F:3 I:1 H:1 F:4 I:1	Y Furan is Extremely Flammable
Cyclohexylamine/ Aniline	$C_6H_{13}N \leftrightarrow C_6H_7N + 6H^+ + 6e^-$	Low Low	H:3 F:3 I:0 H:2 F:2 I:0	Y

No case of a working substance that can operate only in heating or only in cooling was identified since the reason for the failure of a substance was that the maximum cell temperature did not meet thermodynamic requirements, which from the shape of Figure 2, eliminates heating or cooling only operation. Of course, this does not mean that a fluid pair that is not suitable for heat pumps in building space conditioning could not be used in other applications, such as in a refrigeration cycle for a domestic refrigerator. Note, that the method used to down select fluids was derived from first principles and is therefore not contingent upon the analysis or assumptions made in Section 2.2, e.g., this holds regardless of how the cell is modeled.

#### 4. HEATING MODE OPERATION AND PERFORMANCE

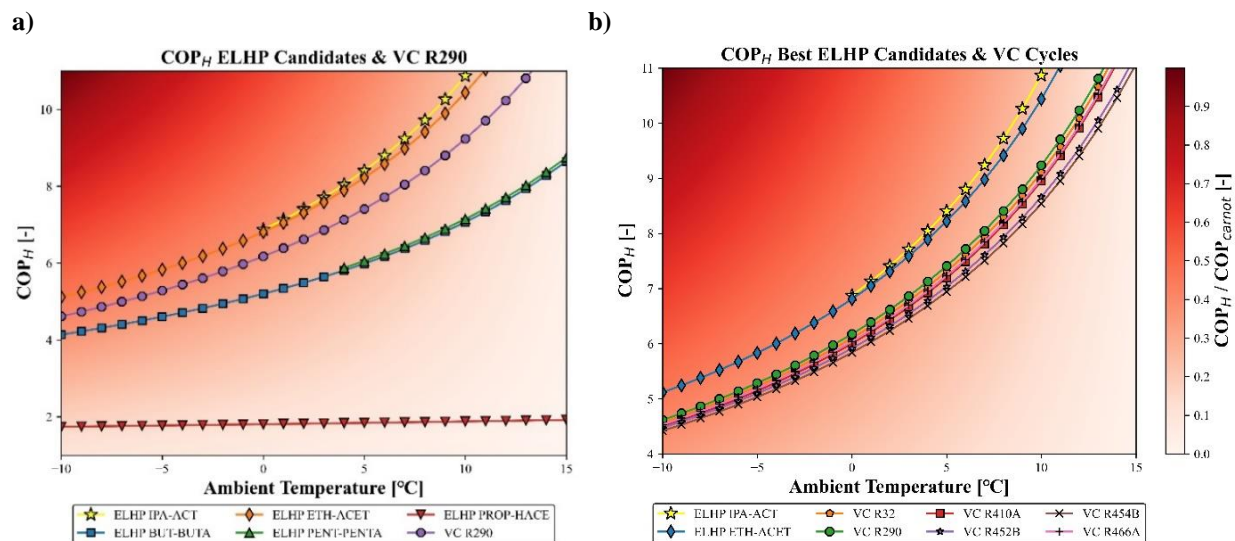
Having down-selected five candidates that can be run in the cycle, it is important to investigate whether these actually offer an improvement over conventional VC cycles. Figure 3 presents a conceptual drawing of the ELHP so that both cooling and heating can be performed.





**Figure 3:** Conceptual drawing of the electrochemical looping heat pump as an externally packaged unit.

A packaged unit can help address some of the safety concerns of these refrigerants such as flammability. With respect to the cycle performance, the coefficient of performance (COP) was calculated using the model presented in Section 2 for the candidates that passed the screening. The heating results are compared to those of typical VC cycles using different refrigerants in Figure 4. It was identified that only two pairs, Ethanol – Acetaldehyde and Isopropanol – Acetone, outperformed the best of the VC cycles (R290) that were considered. The Propylene-glycol – Hydroxyacetone pair was found to have low performance regardless of ambient temperature, which was also found in James et al. 2019. This is attributed to the reactions ( $\Delta G$ ) consuming more energy than the temperature effects and dominating the system performance. The remaining two reactant pairs, Butanol – Butanone and 2-Pentanol – 2-Pentanone were found to have similar performances that were significantly lower than the best two pairs.



**Figure 4:** Thermodynamic performance for heating of (a) ELHP using different reactants (b) the best reactants IPA-ACT, ETH-ACET against different VC refrigerants. The color gradient indicates the 2<sup>nd</sup> law efficiency.

The relative performance differences of the working substances compared to the best VC (R290) cycle performance are shown in Table 5 for their entire operational range. The results include both heating and cooling COP. It was found that ETH-ACET and IPA-ACT were the only candidates that offered improvements over VC technology in both heating and cooling modes of operation.

**Table 5:** Performance characteristics of down-selected ELHP candidates

EWF Pair	Reaction	T <sub>shut,off</sub> H [°C]	% Change VC Heating <sup>†,*</sup>	% Change VC Cooling <sup>†,**</sup>	T <sub>shut,off</sub> C [°C]
Isopropanol/ Acetone	$C_3H_8O \leftrightarrow C_3H_6O + 2H^+ + 2e^-$	-1.6	+ 21.8% [-1.6 to 20 °C]	+ 21.1% [30 to 42 °C]	42
Ethanol/ Acetaldehyde	$C_2H_6O \leftrightarrow C_2H_4O + 2H^+ + 2e^-$	-28	+ 13.5 % [-28 to 20 °C]	+ 11.3% [30 to 45 °C]	45
Butanol/ Butanone	$C_4H_{10}O \leftrightarrow C_4H_8O + 2H^+ + 2e^-$	-11	- 20.4 % [-11 to 20 °C]	- 21.2% [30 to 38 °C]	38
2-Pentanol/ 2-Pentanone	$C_5H_{12}O \leftrightarrow C_5H_{10}O + 2H^+ + 2e^-$	3	- 25.0 % [3 to 20 °C]	- 22.1% [30 to 37 °C]	37
Propylene-glycol/ Hydroxyacetone	$C_3H_8O_2 \leftrightarrow C_3H_6O_2 + 2H^+ + 2e^-$	-11	- 86.2 % [-11 to 20 °C]	- 82.7% [30 to 45 °C]	45

† VC values from EES simulation, R290 used as the baseline cycle. \* Evaluating improvements in heating mode COP<sub>H</sub> at T<sub>H</sub> = 21.1 °C. \*\* Evaluating improvements in cooling mode COP<sub>c</sub> at T<sub>L</sub> = 21.1 °C.

## 5. DISCUSSION AND FUTURE WORK

### 5.1 Temperature Specific Effects on Cycle Performance

The analysis in this paper focused on thermodynamic performance of the cycle that depends only on thermodynamic properties and reasonable assumptions about device efficiencies and heat transfer temperature differences. However, there are other transport properties and effects that impact the operation of the cycle. Although activation, ohmic, and concentration losses have been encompassed in the fuel cell efficiency ( $\eta_{cell}$ ), the overall dependence on temperature was not considered. Future investigations should be directed at (1): cell performance variations due to seasonal operation which can lead to cell temperature variations ( $\Delta T_{cell}$ ) of up to 20 °C, (2) short-term variations due to temperature changes throughout the day ( $\Delta T_{cell} \sim 5$  °C). The authors anticipate that variations will arise from fluctuation in activation losses as shown in Duan et al. 2021, with larger  $\eta_{cell}$  magnitudes in cooling (higher cell temperature) than in heating (Butler-Volmer).

### 5.2 Future Research Directions

The most critical component of the ELHP is the fuel cell. The COP<sub>c</sub> of the cycle was shown in James et al. 2019 to increase linearly with cell efficiency. Although comprehensive work has been performed on the thermodynamics of the cycle (James et al. 2016, James et al. 2019), additional research efforts are still needed in identifying catalysts for the down-selected substances (ETH-ACET and IPA-ACT) and developing robust models that incorporate species transfer in the cell to accurately model its heat generation and management, as well as prototyping the system. Most importantly, however, substantial work is needed in this new field of using electrochemical elements (fuel cells, RFBs) in thermal systems. At the moment, only two relevant thermodynamic cycles exist, the ELHP and the RFB based cycle first presented in Gerlach and Newell (2006). The authors anticipate that this new design space can yield novel systems for energy storage, power and heat co-generation, high-temperature applications, and many more.

## 6. CONCLUSIONS

This paper focused on developing a control and working substance selection scheme for the novel Electrochemical Looping Heat Pump (ELHP) cycle. A broad list of working substances was identified and subsequently down-selected to five candidates. The performance of these candidates was compared to typical vapor compression cycles. It was found that Ethanol-Acetaldehyde and Isopropanol-Acetone were the only candidates that offered a performance improvement. The Ethanol-Acetaldehyde pair achieved improvements of 13.5% for heating and 11.3% for cooling, whereas the Isopropanol-Acetone pair was superior with 21.8% and 21.1% improvements for heating and cooling, respectively. Future research directions and areas of innovation for electrochemical systems were proposed.

## NOMENCLATURE

ACET	Acetaldehyde (-)	HACE	Hydroxyacetone
ACT	Acetone (-)	PROP	Propylene-glycol
BUT	Butanol (-)	P	Pressure (KPa)
BUTA	Butanone (-)	PENT	2-Pentanol
COP	Coefficient of Performance (-)	PENTA	2-Pentanone
ELHP	Electrochemical Looping Heat Pump	PROP	Propylene-glycol
ETH	Ethanol	V	Voltage (Volt)
GWP	Global-Warming Potential	H:	Health, F: Flammability, I: Instability
<b>Subscript</b>			
C	Cooling	high	High-side Pressure
cell	Electrochemical cell	<i>l</i>	Liquid state
<i>evap</i>	Evaporator	low	Low-side Pressure
<i>g</i>	Gaseous state	<i>sat</i>	Saturation
H	Heating	<i>vap</i>	Vaporization

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