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Experimental Investigation of an Electrochemical Compressor Using R1234yf as a Working Fluid

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Abstract

Electrochemical compressor (ECC) offers an oil-free and low-noise alternative to mechanical compression by transporting ions through a polymer electrolyte membrane (PEM). This study presents the first experimental demonstration of electrochemical compression of the low-GWP refrigerant R1234yf using a PEM-based ECC. The objectives are to verify the feasibility of R1234yf transport in an ECC and to identify membrane characteristics that enable stable and efficient operation. R1234yf was mixed with hydrogen and supplied to the anode under controlled temperature, humidity, and inlet pressure, while the outlet pressure was regulated by a back-pressure valve. The voltage–current response was measured for various temperatures between 30°C and 70°C and for different R1234yf/hydrogen mixing ratios. Four membranes with different thicknesses and mechanical properties were compared. The results show that R1234yf can be electrochemically compressed when sufficient hydrogen is present to sustain proton conduction. Increasing temperature lowers the voltage required at a given current. Among the tested membranes, the Gore775 ($15\mu m$) exhibits the lowest ohmic losses and the most stable performance, while thicker membranes lead to significantly higher voltage penalties. This research suggests the potential for future development of heat pump systems leveraging electrochemical compressors.

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Keywords: R1234yf, electrochemical compressor, membrane selection

1. Introduction

Global efforts to reduce the environmental impact of heating and cooling systems are accelerating the adoption of refrigerants with low global warming potential. Heat pumps are becoming a central technology in this transition because they can deliver high efficiency and enable electrification of heating in buildings and vehicles [1]. As heat pump systems spread to residential, commercial, and automotive applications, the choice of refrigerant and the associated compression technology become a key design question. Among the available refrigerants, R1234yf has emerged as a promising hydrofluoroolefin (HFO) because it has a very low global warming potential (GWP), degrades rapidly in the atmosphere, and can be applied to systems that were originally designed for R134a [2]. To fully exploit these advantages in heat pump applications, compression technologies must handle the thermophysical behavior of R1234yf while maintaining high efficiency and stable operation.

Mechanical compressors are still the standard choice for vapor compression in heat pumps and conventional refrigeration systems. However, they suffer from frictional dissipation, lubrication requirements, wearing of

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moving parts, and noise generation. These issues limit efficiency gains and long-term reliability. They also make it difficult to design compact, quiet, and oil free heat pump systems.

To address these constraints, an electrochemical R1234yf compressor (ERC) provides a fundamentally different approach [3,4]. It compresses gas mixtures by transporting ions through a proton conducting membrane under an electrical potential instead of using mechanical displacement. Compression occurs without moving parts, which reduces friction related losses and enables silent and oil free operation. The ERC uses a polymer electrolyte membrane (PEM) and a membrane–electrode assembly (MEA), whose performance has been studied mainly for hydrogen. Electrochemical compression of ammonia and mixed hydrogen–ammonia gases has also been reported, and these systems are already being considered for heat pump application to combine compression and working fluid management in a single device.

Previous work on electrochemical compression has focused almost entirely on hydrogen, with more recent studies extending the concept to ammonia for heat pump application [5]. These studies show that electrochemical compression works for gas mixtures in which hydrogen acts as the charge carrier. They do not examine fluorinated working fluids such as R1234yf. Thermodynamic and electrochemical considerations suggest that R1234yf should also be compatible with electrochemical compression because its molecular structure can support charge transfer and pressure build up across a membrane [6].

Until now, electrochemical compression of R1234yf has not been demonstrated experimentally, and the membrane conditions required for stable operation have not been identified. The present work provides the first experimental validation of an electrochemical compressor using R1234yf and compares several polymer electrolyte membranes. Based on these results, selection criteria are proposed for the design of electrochemical compressors for R1234yf and other fluorinated refrigerants in heat pump systems.

2. Method

2.1. Working principle

R1234yf is an HFO refrigerant with an unsaturated C=C bond in its molecular structure [7]. In the presence of hydrogen and a hydrated PEM, this bond can be protonated under an applied electric field, forming transient cationic intermediates that participate in electrochemical transport.

Fig. 1 schematically summarizes this sequence. The left structure represents neutral R1234yf with its C=C bond. The middle structure shows the protonated cation delocalized over the double bond. This cation accepts an electron and returns to the neutral molecule at higher pressure. In combination, protonation at the anode, migration of the cation, and its reduction at the cathode describe the electrochemical compression mechanism of R1234yf [6].

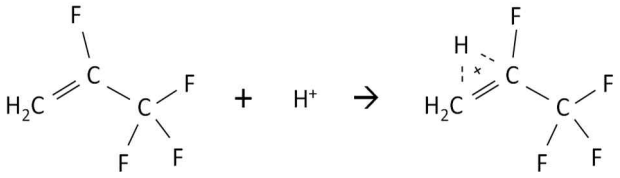

Figure 1. Working principle of R1234yf electrochemical reaction.

At the anode, hydrogen and R1234yf are supplied together. Hydrogen is first oxidized on the anode catalyst to form protons and electrons. The electrons leave the anode through the external circuit, while the protons remain in the anode catalyst layer and in the hydrated PEM.

$$H_2 \rightarrow 2H^+ + 2e^- \ , 2H^+ + 2CH_2CFCF_3 \rightarrow 2CH_3CFCF_3^+ \quad (1)$$

At the cathode, the reverse sequence takes place. The protonated R1234yf species release their protons and return to the neutral molecule. The protons formed in this step are reduced together with the electrons that arrive from the external circuit.

$$2CH_3CFCF_3^+ \rightarrow 2H^+ + 2CH_2CFCF_3, 2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

Fig. 2 shows a schematic of the electrochemical compressor when a mixture of R1234yf and hydrogen is supplied. This electrochemical cycle transfers hydrogen from the low-pressure anode side to the high-pressure cathode side, so the total number of gas molecules on the cathode side increases and the local pressure rises.

R1234yf is compressed together with hydrogen as this pressure builds up, and compression is achieved without any mechanical moving parts.

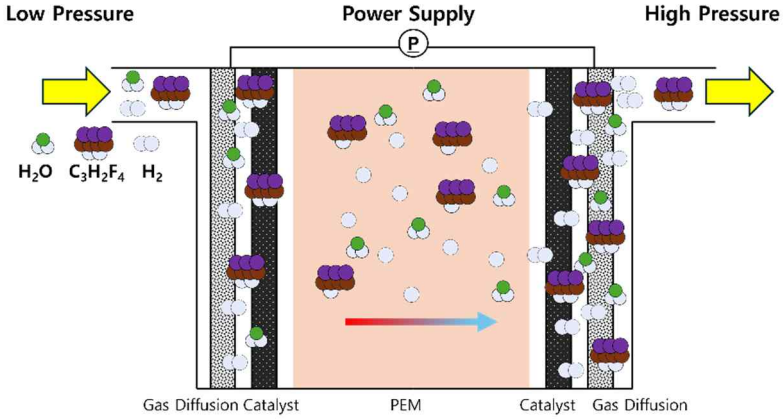

Figure 2. Schematic illustration of electrochemical compression.

The theoretical cell voltage required for this electrochemical compressor is expressed as the sum of a thermodynamic term and additional loss terms [8]:

$$E_{cell} = E_{Nernst} + E_{act} + E_{ohm} \quad (3)$$

Nernst term was determined by the pressure ratio [9,10]. The Nernst voltage was calculated as

$$E_{Nernst} = E_0 + \frac{RT_{EC}}{nF} ln\left(\frac{P_c}{P_a}\right) \quad (4)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, and P_a and P_c are the pressures at the cathode and anode, respectively and n is the number of electrons transferred. This term represents the minimum voltage required to sustain the hydrogen transport that drives compression of the R1234yf and hydrogen mixture.

The ohmic term accounts for the resistive losses in the polymer electrolyte membrane and in the contacts inside the cell. It was expressed as [11]:

$$E_{ohmic} = (R_m + R_{contact})i \quad (5)$$

where R_m is the membrane resistance, $R_{contact}$ is the interfacial contact resistance, and i is the applied current density [12]. Four polymer electrolyte membranes with different thicknesses were tested, so R_m varied mainly with membrane thickness and hydration.

2.2. Experiment setup

Fig. 3 shows the experimental setup used to test the electrochemical R1234yf compressor. R1234yf and hydrogen are stored in separate cylinders and supplied to the system through mass flow controllers. The flow passes through temperature control units and a humidifier or dehumidifier to set the inlet temperature and humidity. The conditioned gas mixture then enters the electrochemical compressor cell, where pressure, temperature and voltage are monitored. A back pressure regulator at the cathode side sets the outlet pressure.

Gas chromatography (GC) plays a central role in this setup. The outlet stream from the cathode is sampled and analyzed to obtain the molar fractions of R1234yf and hydrogen and to check for any reaction products [5]. These measurements are used to verify whether the electrochemical reactions associated with R1234yf compression occur and to confirm that the refrigerant remains chemically stable during operation. In this way, gas chromatography provides direct experimental evidence that the electrochemical R1234yf compression mechanism is realized in the cell.

The cell contains a membrane–electrode assembly with a polymer electrolyte membrane. Four PEM with different thicknesses were tested to examine the effect of membrane thickness on cell resistance and compression performance.

Table 1 summarizes the operating conditions used to validate the electrochemical R1234yf compressor. R1234yf was supplied at an inlet pressure of 1 bar with a fixed volume flow rate of 800 SCCM. Hydrogen was also supplied at 1 bar, and its flow rate was varied from 320 to 800 SCCM to change the mixing ratio between R1234yf and hydrogen while keeping the R1234yf flow constant. The ECC was operated at 50°C and 100% relative humidity so that the polymer electrolyte membrane remained fully hydrated. Four membranes with different thicknesses (Gore 775, N212, N115, N117) were tested under these conditions. This test matrix was used to confirm basic electrochemical compression of the R1234yf and hydrogen mixture and to obtain an initial comparison of cell behaviours for each membrane.

Table 1. Experiment conditions for validation

Parameter		Range	Unit
R1234yf	Inlet pressure	1	bar
	Volume flow rate	800	SCCM
Hydrogen	Inlet pressure	1	bar
	Volume flow rate	320~800	SCCM
ECC	Temperature	50	℃
	Relative humidity	100	%
	Membrane	Gore 775, N212, N115, N117	

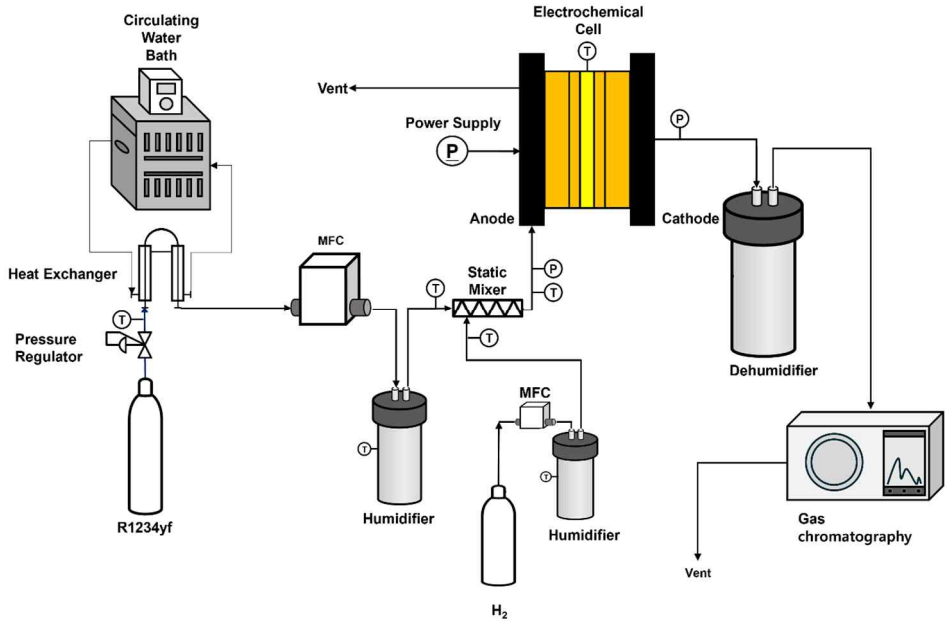

Figure 3. Experimental setup.

Table 2 summarizes the conditions used for the membrane performance analysis. The inlet pressures and flow rates of R1234yf and hydrogen were kept the same as in Table 1, and the relative humidity was again set to 100%. In this case the cell temperature was varied from 30°C to 70°C while using the Gore 775. These conditions were chosen to evaluate how membrane thickness and temperature together affect the cell voltage, the ohmic resistance, and the compression performance of the electrochemical R1234yf compressor.

Table 2. Experiment conditions for membrane analysiss

Parameter		Range	Unit
R1234yf	Inlet pressure	1	bar
	Volume flow rate	800	SCCM
Hydrogen	Inlet pressure	1	bar
	Volume flow rate	800	SCCM
ECC	Temperature	30~70	℃
	Relative humidity	100	%
	Membrane	Gore 775	

3. Results

3.1. Validation of electrochemical R1234yf compressor

Fig. 4 shows the experimental outlet molar ratio of R1234yf to hydrogen as a function of the inlet molar ratio for four membranes with different thickness. According to the overall reaction, the stoichiometric outlet ratio should be 2.0 when electrochemical compression proceeds ideally. For Gore 775, N212, and N115 the measured outlet ratios remain close to 2.0 over all inlet mixing conditions. This indicates that the electrochemical reaction pathway is realized and that the R1234yf and hydrogen mixture is compressed mainly through the electrochemical transport described in the reaction scheme.

The small deviation from the ideal outlet ratio of 2.0 observed for the three membranes is primarily attributed to R1234yf crossover and nonuniform ion transport within the hydrated membrane rather than hydrogen crossover [13]. Hydrogen exhibits a diffusivity on the order of 10^{-5} cm² s^{-1} in hydrated PEM, yet it actively participates in the electrochemical reaction and therefore does not lead to a measurable reduction in the outlet ratio [14]. In contrast, R1234yf does not directly participate in proton transport. As a result, a fraction of R1234yf permeates through the membrane driven by concentration gradients without contributing to electrochemical compression. This R1234yf crossover reduces the effective outlet ratio.

Additional deviation arises from nonuniform ion transport inside the membrane and local dehydration near the electrodes. These effects become more pronounced at high current densities and further limit the effective transport of electrochemically active R1234yf species, leading to a deviation from the ideal value.

The thick N117 membrane shows a very different trend. The outlet ratio remains far below the theoretical value and does not reach 2.0 even at the highest inlet ratio. This behavior is consistent with the large membrane resistance term in the ohmic loss of Eq. (5). The large thickness and severe swelling of N117 lead to high ionic resistance and strong hydration imbalance. As a result, the cell operates in an unstable regime and the electrochemical transport of R1234yf is strongly suppressed. Figure 4 therefore confirms that electrochemical compression of R1234yf is feasible, but also that stable operation requires membranes with moderate thickness and well controlled hydration [15,16].

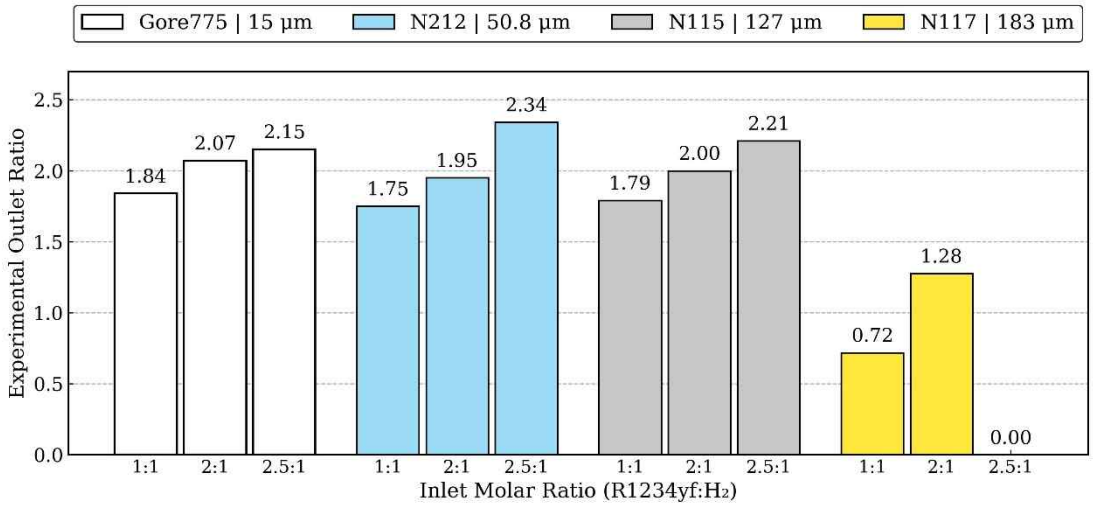

Figure 4 Experimental outlet molar ratio at different inlet molar ratios for four different membranes.

3.2. Effect of membrane thickness and temperature on cell voltage characteristics

Fig. 5 presents the current and voltage characteristics of the electrochemical R1234yf compressor and illustrates how membrane properties and operating temperature affect the terms in the cell voltage expression. At low current density the measured voltage is close to the thermodynamic Nernst voltage plus a small activation loss, as described by Eq. (3) and Eq. (4). The curves for different membranes start from similar intercepts, since the hydrogen partial pressure ratio is fixed and the Nernst term is therefore almost the same.

As the current density increases, the voltage rises almost linearly. In this region the slope is dominated by the ohmic term in Eq. (5). Thicker membranes such as N115 and especially N117 have a larger membrane resistance, so the quantity in parentheses in Eq. (5) becomes larger and the voltage increases more rapidly with current. Gore 775 shows the smallest slope, which indicates low ohmic loss and good proton conductivity under fully hydrated conditions. This trend agrees with the membrane thickness and swelling behavior inferred

from Fig 4.

The temperature dependent curves in Fig. 5 (b) show that the slope of the voltage–current relation decreases as temperature increases. The Nernst term changes only slightly with temperature because the pressure ratio is fixed, while both ohmic and activation losses decrease. Higher temperature improves ionic conductivity in the membrane and accelerates the electrode reactions, so the total resistance in Eq. (3) becomes smaller [17]. As a result, the cell requires a lower voltage to deliver the same current, and the power consumption for a given compression level decreases [18,19]. Fig. 5 therefore links the experimental current–voltage behavior directly to the Nernst and ohmic terms and confirms that thin, well hydrated membranes operated at elevated temperature provide the most favorable conditions for electrochemical compression of R1234yf.

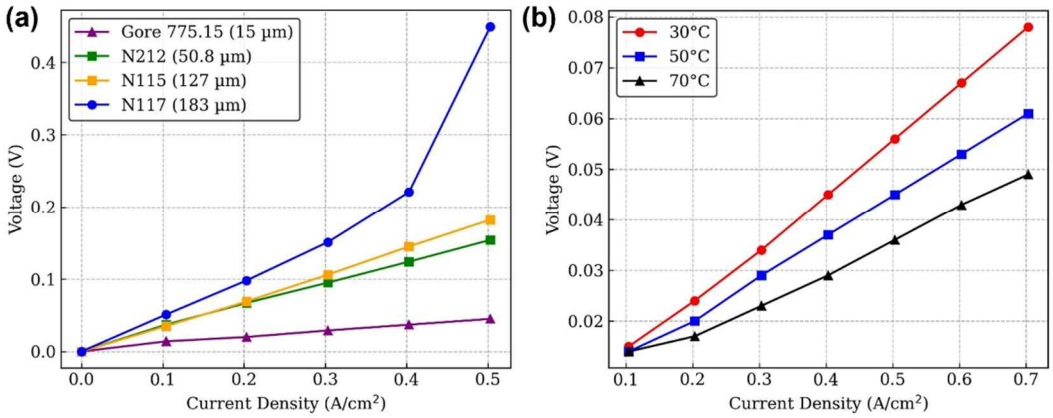

Figure 5 I-V characteristic. (a) four different membranes. (b) temperature of Gore 775.

4. Conclusion

This study experimentally demonstrated that an electrochemical compressor could compress a mixture of R1234yf and hydrogen. Gas chromatography confirmed that R1234yf remains chemically stable during operation and that the outlet composition follows the stoichiometry expected from the proposed reaction scheme. These results show that electrochemical compression is a feasible option for refrigerants with low global warming potential when hydrogen acts as the charge carrier.

The comparison of four polymer electrolyte membranes showed that membrane properties strongly influence cell performance. Gore 775, which has the smallest thickness, produced outlet molar ratios close to the theoretical value and the lowest cell voltage at a given current. N212 and N115 also supported electrochemical compression of R1234yf, but with higher ohmic loss. N117, the thickest membrane, exhibited large deviations in outlet ratio and unstable operation due to its high resistance and poor hydration control. These trends are consistent with the dependence of the ohmic term in the cell voltage on membrane resistance.

Temperature sweeps with the selected membrane showed that increasing the operating temperature reduces both activation and ohmic losses while the Nernst term remains almost unchanged. As a result, the cell voltage required for a given current decrease and the electrical energy needed for compression is reduced.

Overall, the results identify thin and well hydrated membranes as a key requirement for electrochemical compression of R1234yf and indicate that moderate temperature operation further improves performance. The findings provide a basis for membrane selection and operating strategy in future electrochemical compressors designed for R1234yf and other fluorinated refrigerants in heat pump systems.

Nomenclature

ECC	Electrochemical compressor	E	Voltage (V)
PEM	Polymer Electrolyte Membrane	R	Gas constant
HFO	Hydrofluoroolefin	T	Temperature (°C)
GWP	Global Warming Potential	F	Faraday constant
ERC	Electrochemical R1234yf Compressor	P	Pressure (bar)
MEA	Membrane Electrode Assembly	i	Current (A)
T_{EC}	ECC temperature (K)	E_{act}	Activation overpotential (V)
E_{Nernst}	Nernst voltage (V)	E_{ohm}	Ohmic overpotential (V)

P_a	Anode pressure (bar)	P_c	Cathode pressure (bar)
R_m	Membrane resistance (Ω)	$R_{contact}$	Contact resistance (Ω)

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