Using Proton Exchange Membranes (PEMs) to Revolutionize Refrigeration

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ABSTRACT

Xergy's invention characterizes a new category of refrigeration, cooling and heat-pump compressor for vapor-compression cycles. This new compressor is based on Proton Exchange (or Polymer Electrolyte) Membranes (PEMs), is termed an Electro-Chemical Compressor (ECC), is essentially a proton-pump, has no moving parts, is more efficient than existing technology and uses green refrigerants. This is a revolutionary and disruptive technology in many markets and industrial sectors.

Xergy's ECC invention (project name: Kuel-cell^{TM}) is a sealed, continuous cycle, gas compressor only requiring electricity to operate. The continuous cycle presents hydrogen to the anode, followed by lightly compressed hydrogen at the cathode. In so doing, a polar refrigerant can be propelled, as if a mechanical pump, but within the "Solvation-shell" (aka "Solubility-shell") of the protons.

ECC's are well established from a technology stand-point and have demonstrated Exergetic efficiencies in excess of 75%. Thus devices and appliances utilizing ECC's are (i) significantly more efficient than traditional, motor-driven compressors. ECC's can (ii) operate with "green" refrigerants (ie. do not employ ozone depleting refrigerants). Additionally, since there are no motors or moving parts, they are (iii) noiseless and (iv) vibration free, (v) offer simpler manufacturing and (vi) less maintenance whilst in operation. They are also (vii) modular, due to their motor-less form-factor, and are (viii) scalable. Importantly they also have the (ix) durability and (x) longevity to perform as well, if not better, than existing technology. There are numerous other second-order benefits depending on the specific applications in which they are employed, for instance silent, low-maintenance, high-efficiency, highly effective, distributed-cooling for buildings is now a possibility.

Thus the workhorse of the refrigeration, cooling and heat-pump industry, for over 100 years (the venerable, yet polluting, electro-mechanical compressor, made in the 100's of million each year) is set to be replaced by a modern, clean, green alternative.

This paper seeks to explain how ECC's operate and explores several commercial applications such as heat pump and within refrigeration systems.

Keywords: Kuel-cell, Refrigeration, Air-Conditioning, PEM, Heat-pump

1 INTRODUCTION

Xergy's technology utilizes the ability to electrochemically move moderately pressurized hydrogen, as protons, across a (PEM) membrane to propel refrigerant molecules through that same membrane via association and solvation, within the proton flux. The pressures required are significantly below that used to (a) compress hydrogen for storage and (b) below those generated by commercial hydrogen generators.

One key element of hydrogen compression is that protons, migrating across the membrane, carry between 4 and 20 molecules of a polar fluid (such as water) through the membrane with them, in what is termed a "solvation shell". This enables the ECC "cell" to effectively act as a pump, transporting a working fluid (eg. a refrigerant) from the low pressure side of the cell to the high pressure side.

A wide range of refrigerant molecules can be "pumped" across the membrane, as long as the refrigerant molecule has some degree of polarity. Refrigerants listed in Xergy's patents include a range of polar compounds such as water, ammonia, methanol, ethanol and combinations of these compounds as appropriate.

2 THIS IS NOT A FUEL-CELL

PEM research to date has focused on water management (ie. control or prevention) and maximizing proton mobility for applications in fuel-cell systems. The ideal water solvated fuel-cell PEM would have massive levels of very tightly bound water for hydration where protons "hop" through the membrane, from one water molecule to the next (Grotthuss mechanism), with the water staying immobile.

In an ECC, the goal is rather different. It is to have a highly mobile solvent that travels with the proton as it is pulled through the membrane (osmotic drag) toward the cathode, via the applied voltage on the cell. The solvent, which in this case can be water, would exit on the cathodic side at higher pressure. Thus water is the working fluid (ie. refrigerant), and rather a good one, for a standard vapor-compression, heat-pump cycle that can operate at temperatures above zero and below 100 Celsius.

Since the working fluid flux (WFF) of an ECC cell is critical to use in refrigeration systems, the higher the WFF, the more effective the unit will be for its electro active area (EAA), which translates directly into product-value and reduced manufacturing cost. This is quite different to the needs of other forms of hydrogen compressor and makes Xergy's technology unique, requiring cross-functional knowledge between the disciplines of electro-chemistry and thermodynamics.

3 ELECTRO-CHEMISTRY

The movement of hydrogen across the membrane is the sum of two hydrogen half cells; oxidation of hydrogen gas at the anode (H2 → 2H+ + 2 electrons) and reduction of protons to hydrogen gas at the cathode (2H+ +2 electrons → H2). The electro-potential for this movement to occur is 0 volts since it is the mirror image reaction on each side of the membrane.

Thermodynamically, to increase the pressure of Hydrogen by 10 times, on the cathodic side, requires 0.029 V plus the isothermal enthalpy increase. In such a situation, one would have exceedingly high efficiency but virtually no flow. In order to increase the mass transport of the hydrogen one has two choices: (a) to increase the cell area or (b) to increase the voltage driving the kinetics of the reaction. One has an operating window of voltage where the hydrogen flow increases at the expense of efficiency, until the voltage is driven high enough to produce other electrochemical reactions (eg. electrolysis or destruction of the membrane and cell components). There are two competing setups: (i) high efficiency requiring low voltage and very high membrane area, or (ii) lower membrane area with higher voltage resulting in lower efficiency. One therefore has to choose an operating voltage that provides the required mass-transport, at an acceptable cost effective position, while balancing operating efficiency against fabrication cost. This of course suggests a "sweet-spot" for any given set of requirements.

One of the properties of ionomers (PEM), and in particular of Perfluorosulfonic Acid (PFSA) membranes, is their ability to absorb polar-liquids, and transport ions through these liquids under an electric field. An ECC would use the appropriate ionomer to transport hydrogen along with a working fluid from a region where there is a heat source, to a region where it can release thermal energy efficiently. Its subsequent reintroduction to the heat source region, where it can reabsorb more heat again, completes the vapor compression, heat-pump cycle.

Contributing factors to the net overall polar-proton associated material-transport, are (i) the solvation shell drag through the cell, (ii) back diffusion from the cathode, and (iii) the diffusion of any polar-liquid in the feed stream through the anode. Proton associated liquid (solvation) transport is a function of cell-current and the characteristics of the membrane and the electrodes. Liquid drag refers to the amount of polar component that is pulled by osmotic action along with the proton. Between 1 and 20 molecules are dragged with each proton in what is termed a "salvation shell." As a result, the ion exchanged can be envisioned as a solvated proton, H+ (Polar)n. A polar proton associated refrigerant (eg. water) is transported across the membrane and exits the membrane when protons are reduced to form pressurized hydrogen gas at the cathode releasing the associated solvation shell.

This pressurized hydrogen, in a flow channel, sweeps the solvent (eg. water) permeating through the cathode, and subsequently further pressurizes this working fluid, as it flows out of the cathode chamber.

It is important to emphasize that the presence of a solvation shell is not only central to fluid mobility (ie. refrigerant flow), but also enables the movement of a single proton to be leveraged into the movement of multiple molecules (up to 20) of a refrigerant compound. This has a very significant effect on the overall efficiency attainable for fluid pumping (and subsequent compression). Solvation (and a salvation shell) occurs spontaneously for any highly charged species or a high charge density material such as a proton. The higher the charge density of an ion, the larger the solvation shell and the stronger they are bound. Solvation results in delocalizing the charge and stabilizing it. Higher pressure and low temperature favor solvation since they increase the interactions between the charged species and the solvent. When a solvated species moves through a viscous material (or a tunnel, such as in Nafion® membranes) there will be a tendency for the solvent molecules to be pulled away by collision either with the viscous fluid or the walls of the tunnel.

4 COMPRESSION RATIO

Xergy completed the construction of a low-fidelity, multi-cell, demonstration unit on 2012 (project-name "Homer", see Figure 4.1).

Figure 4.1 – "Homer" Demonstration Unit

Several preliminary tests measuring pressure output across eight (8) single Membrane Electro Assembles (MEAs), connected electrically in series and plumbed in parallel, have been conducted.

Measurement of current-versus-voltage and gross pressure-versus-voltage under various conditions have been conducted. Since the focus recently has been to develop a compressor for a Hybrid Water-Heater (HWH – a domestic water-heater relying on a heat-pump rather than a resistive-heater, eg. GE's GeoSpring) application, the cells were operated under simulated conditions and with the following graphs (Figures 4.2 & 4.3) as examples of the type of data able to be generate:

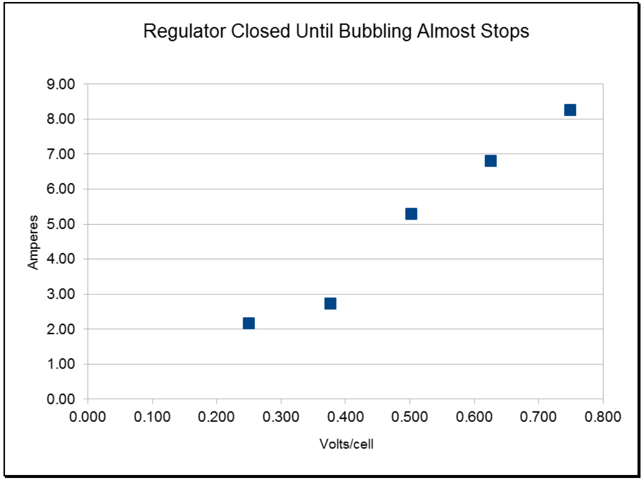

Figure 4.2 - current-versus-voltage

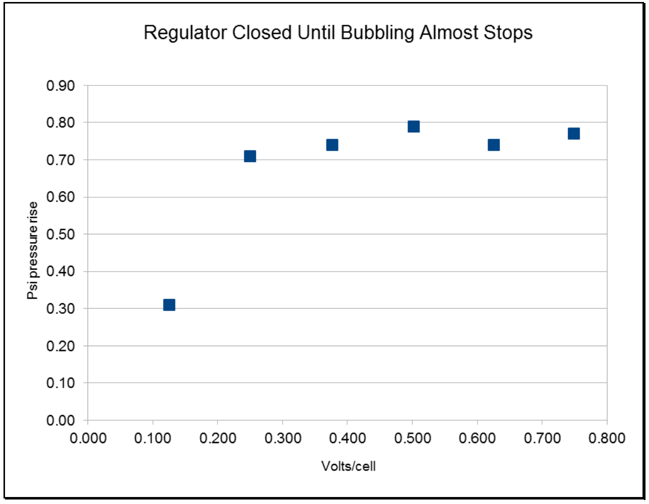

Figure 4.3 - gross pressure-versus-voltage

The absolute pressure rise, demonstrated across the single MEA in "Homer", is 7.75 psi on the cathode, with near vacuum conditions on the anode. This of course can be multiplied further with the use of more cells plumbed in series.

Tests involving "Homer" have demonstrated a compression ratio of >15 based on differential pressure readings across the regulator. Water vapor pressure, at the ambient conditions, is easily and reproducibly achievable across a single MEA.

Many design issues were uncovered while running these tests. At higher pressures it is believed that the electrical conductivity between the Gas Diffusion Layer and the metal cell holder is being compromised resulting in increased contact resistance and thus reduced current.

This compression data should be considered only as illustrative and not a definitive basis for evaluating this technology. There are significant opportunities for improved performance with higher-fidelity prototypes.

5 APPLICATIONS

Electrochemical compressors have been proposed, by other companies for several years, for use mainly in hydrogen refueling stations, to pressurize hydrogen gas for storage. They have also been applied into novel refrigeration systems to pressurize hydrogen for absorption into metal hydrides.

The core technology being proposed by Xergy is to use PFSA membranes in an ECC assembly to replace the mechanical compressor component (ie. the motor) in a typical 4-stage vapor compression cycle system as shown schematically in Figure 5.1.

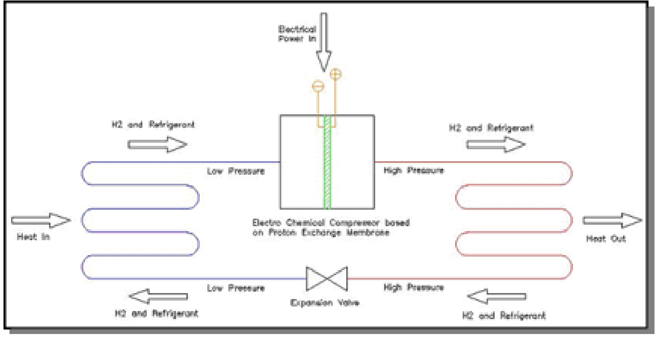

Figure 5.1 – Standard Carnot Cycle with ECC

These compressors are: (a) more efficient (ie. have inherently high COP's) than conventional compressors, (b) motor-less and therefore more reliable, vibration free and noiseless. In addition to the previous general advantages for ECCs, when they are used in a vapor phase compression cycle, there are additional advantages of: (c) not using CFC or derivatives, and therefore being non-GHG, environmentally-friendly and (d) are modular and scalable, (e) can operate very efficiently at partial loads, and (f) can be designed to different form-factors to accommodate other design criteria for an appliance or product.

The operating range of a specific ECC depends on the refrigerant used. To date, Xergy Inc. has patented ECC systems and components employing water, methanol and ammonia as refrigerants. Thus, heat pumps operating at sub-zero temperatures (typical in household freezers and industrial refrigeration systems) are feasible utilizing Ammonia as a refrigerant. Heat pumps operating at conventional room temperature such as window air conditioning units could use ammonia or water. With heat pumps actually used in heating water to 140 F (used in HWH) utilizing water as the working fluid.

6 OPERATING EFFICIENCIES (COP)

Kilicarslan and Muller, in a published comparative study of water, and a series of other materials as refrigerants, concluded that water has the highest inherent Coefficient of Performance (COP – an important thermodynamic term) with low temperature lift. In a medium temperature lift of 28 deg F, the COP is still one of the highest only being surpassed by ammonia.

The absolute temperature range where water can be an effective refrigerant is bounded on the low side by mass transfer at low pressure. This is both an engineering and cost constraint since excessively large pipes may be needed for sufficient mass flow. Operation at 60 to 70 degrees F is believed to be feasible. The high side is primarily constrained by safety but is easily in excess of 400 deg F. in a mechanical system. Absolute heat-flux is a function of mass-per-hour, of working fluid, and the materials of construction which is application specific.

7 MODELING

In general, Xergy's modeling has concluded that 30% to 50% improvement in COP is feasible versus conventional mechanical compressors (depending on the specific details of the application). Improvements of one magnitude or more (ie. >10x) in COP's is also feasible in smaller devices compared to conventional thermo-electric (Peltier) systems.

Initial work by PROSIM (www.prosim.net) to develop a module for Xergy, that correctly models the ECC, and is best described as "isothermal compression followed by isobaric heating", is incomplete. PROSIM's software has limited ability to include entropy changes in their simulations. The isentropic inefficiency of the ECC is manifested as heating and is observed in operation primarily as ohmic losses and activation energy (over potential). The current simulation approximates an ECC as a multi-stage mechanical compressor with inter-cooling. That simulation is based on standard components in PROSIM's software but is penalizing the ECC with excessive power requirements. The simulation correctly has lower output temperature vs. a typical mechanical compressor but the energy of heating (and shed to the coolers) is included in the power demand. It is proposed that the correct power requirement for an ECC is between the gross and net (gross being the heat shed by intercoolers) compressor power.

8 CONCLUSIONS

Based on case studies presented and multiple client engagements, using water as the working fluid and assuming a 90% efficient DC power supply, COP improvements on the order of 30% to 56% are attainable in a non-optimized commercial heat-pump system utilizing ECC. Even higher performance can be expected with systems optimized for this technology (ie. correct expansion valve, heat exchangers, power supplies etc.).

For the HWH application, the ECC needs to provide 4 lbs/hour of working fluid-water throughput to match the heat output or power input of a HWH system and other targets such as water temperature set point and ambient air temperature. This is equivalent to 350 mmols m-2 s-1 rated water flux for Xergy's advanced composite membrane.

The ECC operates essentially as an isentropic, multi stage compressor with inter-cooling.

Polarization curves are available based on commercial fuel-cell MEAs, used in compressor mode, that allow a wide range of design operating point selections. In these examples, cell operating points lower than 0.3 V per cell at 950mA/cm2 where chosen which appear to be consistent with the efficiency assumptions utilized in the system modeling effort used in PROSIM.

There appears to be significant opportunities to reduce costs and improve system performance by using alternative ionomers, and composite membrane constructions, to those commercially available today. There also appears minimal sensitivity to catalyst loading changes of 3X on the cathode which implies major opportunities to reduce catalyst loading and therefore costs in future assemblies.

On the basis of the design work to date, and real experimental data produced using early prototypes and demonstrations units, there is confidence that commercial systems are not only feasible, but ultimately provide compelling value added benefits in many applications.

Cell designs have been developed using a DC power supply of 3.3, 5, 6, 12, or 24V with a current demand on the 240V. These power supply voltages are consistent with typical bus voltages generally available (ie. telecom and computer industry).

From a safety standpoint, it is important to realize that the total volume of gases employed in these systems is relatively low, with as much potential for exposure and risk as, say, a the gas volumes in a household aerosol or cigarette lighter. Xergy has designed and patented a secondary steel enclosure for the system that provides hermetic sealing.

In addition to operating on DC bus voltages, this technology is noiseless, modular, and scalable. ECCs can also be proportionally controlled for modulating heating. The complete benefits for using ECC are still being recognized. In addition to improved efficiency, modularity, and vibration-free ECC act similar to resistive loads which do not produce in-rush currents, which can have a significant impact on a building's power costs and control strategy. The COP, taken in conjunction with other inherent and second-order benefits, along with additional specific improvements identified for heat-pump system (such as eliminating surge currents, simplified electrical controls, etc.) provide a compelling case for this technology.

9 REFERENCES

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