

PEM Fuel Cell Multiphase System

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ABSTRACT: A multi-phase thermal fluid has been investigated and developed for a Proton Exchange Membrane (PEM) fuel cell. The system has been developed specifically for a 1.5kW stationary PEM to enhance the thermal stability within the system, and to improve the reliability and electrical efficiency. The multi-phase system is proposed to act as a novel method of heat recovery to buffer fluctuations in load and reduce parasitic loading by increasing fluid thermal capacitance and reducing flow velocities.

The multi-phase thermal system is made up of a two component fluid. Phase change materials have been selected and processed using a novel method of micro-encapsulation. These have been mixed and suspended in a working fluid to form a slurry which was pumped around the system. Investigation into the additional thermal capacitance and improved thermal conductivity of the slurry was undertaken to assess reductions in pumping loads. Thermal analysis and experimental tests have revealed significant increase in thermal buffering which offers the potential to enhance system stability. This in conjunction with reduced pumping power could improve the overall electrical efficiency of the fuel cell. This work has built upon previous thermophysical development of multiphase fluids and has developed a suitable microPCM slurry for further experimental tests with a fuel cell.

Keywords: PEM Fuel Cells, Microencapsulated Slurry, Phase Change Material (PCM)

1. INTRODUCTION

Hydrogen and fuel cells are seen by many as key technologies for the 21st century, enabling clean efficient electricity production and heat from a range of primary energy sources. Fuel Cell Systems (FCS) in particular are a promising type of on-site power generation technology that offers modularity, efficient operation across a wide range of load conditions, minimal environmental impact, and opportunity for integration into cogeneration systems that can vastly improve the Coefficient Of Performance (COP). Cogeneration systems simultaneously provide power and heat and offer a number of advantages including economic benefits, utilisation of sustainable energy resources, and reduced environmental impact. The advent of fuel cell cogen systems promises to make these advantages available in applications that were not previously well suited, in particular small scale stationary facilities.

The stationary FCS has many challenges to overcome on its path to commercialisation, ranging from gas production, distribution and storage to public awareness and acceptance. Its cogeneration and suitability characteristics are well suited to stationary energy utilisation patterns; however, the system must be reliable, efficient and economically viable. The thermal management within the FCS is a function that should operate effectively and efficiently, to distribute heat around the system and to harness the thermal energy for cogeneration. Currently the thermal

management system uses water as its thermal carrier fluid, however, it is proposed that this is replaced by a multi-phase fluid to reduce parasitic loading (hence improve the overall electrical efficiency) and assist thermal stability.

This paper provides an overview of the recent developments in multi-phase fluids with particular focus on the development of a Microencapsulated Phase Change Material (MicroPCM) for a fuel cell. MicroPCMs are small particles of phase change material that are encapsulated in a thin plastic shell and suspended in a single phase working fluid (water). The latent heat associated with phase transition from solid-liquid under heating, and liquid-solid under cooling, can enable improved thermal capacitance and heat transfer over that of a single phase fluid. Microencapsulation of the PCM allows the continual separation of the melted core material from the circulating carrier fluid and thus the potential to avoid collecting or deposition of the core material in undesirable areas of the system^[1]. Figure 1, illustrates the cross section of a typical microPCM particle.

The objective of the multiphase fluid is to serve as both an energy storage and heat transfer medium, to reduce loading on separate heat transfer and storage media. Many conventional systems using the sensible heat of a single phase working fluid often operate at a high volume flow rate. As a result, the system can consume a large amount of pumping power. The slurry is used primarily to reduce parasitic loading from pumps and mechanical valves by reducing the flow rate of the working fluid. This is

achieved through improving the working fluid thermal capacity and heat transfer characteristics that in turn can improve heat exchanger efficiency. Additional slurry characteristics that are beneficial to the system include; thermal safety buffering, to reduce the risk of overheating that could lead to stack damage; improved heat exchanger lifetime from reduced rapid temperature changes that cause expansion and contraction resulting in fatigue damage.

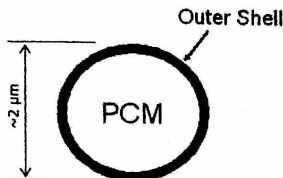


Figure 1: MicroPCM Particle Cross-Section

MicroPCM Background

Over the past decades, many researchers have shown the advantages and possible utilisation of encapsulated PCM in small capsules. A study concerning the thermal use of MicroPCM slurries was reported in 1979 by Mehalick and Tweedie. Since 1983, NASA have demonstrated the effectiveness of this novel coolant in significantly enhancing effective thermal capacitance to enable reduced weight and volume of thermal storage in space craft^[1]. Kasza^[2] 1985, reported that the convective heat transfer coefficient and thermal capacity of a working fluid was increased with the concentration of MicroPCM in the slurry. Since this period, further work has been published concerning the feasibility of using MicroPCM to enhance the convective heat transfer in a working fluid [Roy (1991,1997), Colvin (1992), Geol (1994), Choi (1994) and Yamagishi (1999)] and various assessments of thermal system design.

The solar industry has previously been targeted as a promising area for MicroPCM slurries. Kasza and Chen^[2] first suggested the use of slurry integration to improve solar energy or waste heat utilisation, however, to date no commercially available systems utilise these mid temperature slurries. Problems in the past have included agglomeration of the particles when left stationary for prolonged periods and cell degradation from pumping shear forces. Current slurries now can incorporate surfactant that can render the particles to be neutrally buoyant within the slurry and prevent agglomeration. Cell degradation has been tackled by improved encapsulation methods and capsule material, combined with the use of capsule friendly pumps that have reduced shear such as moyno progressive cavity^[1] and diaphragm pumps

MicroPCM slurries have the potential to be of greater significance in stationary FC cogen systems as they are highly dependent on efficient use of

energy and are hindered by parasitic loads that serve to reduce this efficiency. A multiphase fluid has the potential to reduce the parasitic loading whilst providing other advantages such as thermal stability and buffering, reduced plant and heat exchanger size and cost.

The rest of this paper analyses the Fuel Cell and Thermal System, and indicates the development process undertaken to produce a microPCM suitable for use with the fuel cell.

2 PEM FUEL CELL SYSTEM

2.1 Fuel Cells

In principle, a fuel cell operates like a battery. Unlike a battery, a fuel cell does not run down or require recharging. It will produce energy in the form of electricity and heat as long as fuel is supplied. A fuel cell consists of two electrodes, called the Anode and Cathode, sandwiched around an electrolyte. Hydrogen passes over the cathode and oxygen over the anode, generating electricity, water and heat.

2.2 Fuel Cell Background

The proton exchange membrane (PEM) fuel cell is the most promising and rapidly advancing fuel cell technology for small-mid size stationary applications. It was first introduced in the late 1960s with the Gemini Space Program, and was neglected thereafter until the 1980s due to high costs^[4]. Recent improvements in cost and performance have been achieved during the last decade that allow PEMs to be considered as realistic alternative power sources with high fuel efficiency and low emission characteristics. Many prototypes that are currently being tested and demonstrated for stationary use, extract hydrogen from propane or natural gas by a reforming process.

2.3 Fuel Cell Thermal Management

The main task of the fuel cell thermal management strategy is to provide the FC components with a sufficient cooling load to meet their requirements. It must also maximise the cogen function of the system in order to maximise the system efficiency.

Figure 2. illustrates the fuel cell thermal management system (TMS) and its interactive components considered by this project. The fuel cell system comprises of four main sections:

- Fuel processing system (FPS), which converts a hydrocarbon fuel such as natural gas into a hydrogen-rich mixture.
- Fuel cell stack (FCS), which generates dc current from hydrogen-oxygen electrochemical reaction; heat is exchanged via the water cooled stack circuit and from the cathode return stream that has been dehumidified.
- The Co-generation system, which acts as a thermal manager (TMS) to provide sufficient

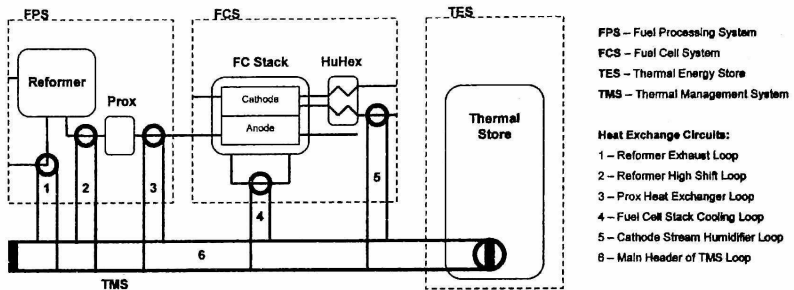


Figure 2: Sketch of FCS components and Multiphase circuit

cooling to the components and transfers heat generated by the fuel processing and stack.

- Thermal store and distribution, provides storage of excess thermal energy to supply and meet periods of user energy demand.

The thermal management system of the fuel cell consists of six heat exchangers and can be identified in figure 2. Within the FPS, heat exchangers were located after the reformat high temperature shift converter, the preferential oxidation reactor (Prox) and at the reformer exhaust. The FCS had a heat exchanger situated in the deionised water circuit that cools the stack and another in the cathode air exhaust. The final heat exchanger is located in the thermal store that transfers the energy from the aforementioned heat exchangers.

The heat transfer circuit consisted of five heat exchangers for extracting heat, however only two of the components were major contributors to the thermal cogen supply. For the purpose of the MicroPCM slurry assessment these loads were assumed to be $0.5kW_{TH}$ from the reformer exhaust and $2.5kW_{TH}$ from the FC stack at $65^{\circ}C$. The flow and return temperatures for the thermal system $65^{\circ}C$ and $40^{\circ}C$ respectively.

Based on the Fuel cell operating characteristics, the design of the Multi-phase fluid for the thermal system was established at $65^{\circ}C$ and $40^{\circ}C$, flow and return temperatures respectively.

3 MicroPCM DEVELOPMENT

3.1 Phase Transitional Temperature

The phase transitional temperature for the PCM may be defined as the peak temperature that phase change occurs. In order to create a microPCM that was suitable for use with the Fuel Cell it was important that the phase transitional temperature was tuned to the system. This meant that in one complete cycle of heating and cooling phases, maximum melting and re-crystallisation of the PCM could be achieved.

Thermal Analysis (TA) measurements were undergone on currently available n-eicosane

microcapsules with various phase change temperatures. The TA technique involves the determination of temperature-time diagrams, or the heating and cooling curves, recording the melting and freezing of the sample.

The test temperatures were set to simulate the fuel cell flow and return temperatures. From the TA investigation, the optimum peak transitional temperature was determined at $55^{\circ}C$. This temperature would be a design criterion for the phase change material.

3.2 Development Process

The approach depicted in figure 3, shows the steps taken to produce suitable microPCMs for use with the fuel cell and achieve the following stated goals; selection of a phase change material with the desirable phase transition and melting point, good enthalpy and thermal homogeneity, minimal supercooling and good durability for pumping.

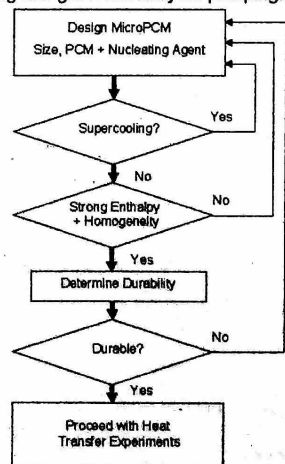


Figure 3: MicroPCM Design and Experimental Approach.

3.3 Encapsulation Process

Traditionally, encapsulation techniques have been taken from the printing industry. This typically uses Melamine-formaldehyde as the encapsulating shell type. Capsule size using this method of encapsulation was usually in the region of 10-100 μm in diameter. A different type of encapsulation method was used for this investigation to produce smaller microcapsules at 1-10 μm in size and with a different shell type. The understanding was that a more colloidal slurry could be produced with reduced tendency for separation. The process used was acrylic polymerisation which formed durable acrylic shells encapsulating the PCM. The process of acrylic polymerisation is depicted in the following figure 4^[6].

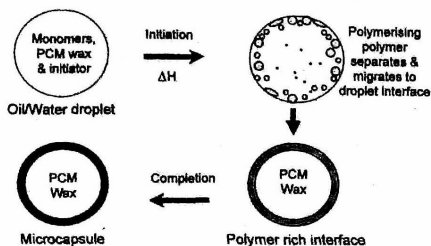


Figure 4: Acrylic Polymerisation

In order to use this encapsulation process, a requirement that had to be considered in the selection of PCM was their solubility. For the process to take place the PCM had to be water insoluble.

3.4 Supercooling

Supercooling is a common problem with encapsulated PCMs. This phenomenon may be considered as a process that brings the temperature of the PCM down to less than its phase change temperature without it forming crystals and storage of latent heat. Recent studies and patents have shown that the effects of supercooling can be significantly reduced with the inclusion of a nucleating agent^[7].

3.5 PCM Selection

A wide range of paraffin's was considered for encapsulation. On a thermophysical basis, they were distinguished by phase transitional temperature, latent heat capacity, density and boiling point. With an economic bias they were also considered by cost and availability.

Materials; Hexadecanol, Myristic Acid, Octadecanol and a Paraffin Composite met the above criteria and were considered for further development. Initial problems showed poor encapsulation, significant supercooling tendencies and particle separation. Hexadecanol Proved to have a phase transitional temperature that was too low at 50°C and suffered from supercooling. Myristic Acid showed poor encapsulation, however with the addition of a

nucleating agent with the PCM, it showed reduced supercooling effect. Both the Octadecanol and Composite paraffin, with the inclusion of a nucleating agent (based on patent^[7]) showed positive enthalpy characteristics. The nucleating agent used was Stearic Acid.

Tests based on the development approach, figure 2, were completed for each of the PCMs; however, the Paraffin Composite was the most promising and is the focus of the rest of this paper.

3.6 Thermal Evaluation Methodology

Experimental tests used to evaluate the microPCM included measurements of thermal characteristics and enthalpy with Differential Scanning Calorimetry, Capsule strength with Thermal Gravimetric Analysis, and particle size with Laser Diffraction.

3.6.1 Particle Size Analysis

A HELOS laser diffraction machine was used to give a quick and reliable analysis of the particle sizes of the encapsulated PCMs under development. Figure 5, illustrates the particles size distribution for the paraffin composite. The mean particle size was 1.4 μm .

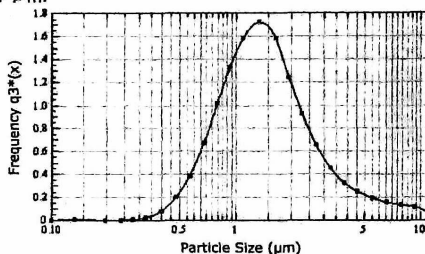


Figure 5: Particle Size Analysis

The HELOS used light diffraction of a laser beam on the sample/microPCM particles to create a pattern which is measured by an array of detectors. Software provided with the HELOS was used to obtain the particle size distributions.

3.6.2 Differential Scanning Calorimetry (DSC)

Energy storage and release capacity of the MicroPCM was measured using a Differential Scanning Calorimeter-Perkin Elmer, Pyris 1. The apparatus measured the heat flow through the sample pan compared with the heat flow through a reference pan as a function of the temperature. Heat flow increased when there was any phase change occurring in the sample pan. As seen in figure.5, any phase transition in the sample was identified as a peak of heat flow. The area between the curve and the baseline of this peak represents the latent heat of fusion of the phase transition. Any positive heat flow value indicated the heating phase of the sample and negative values the cooling phase.

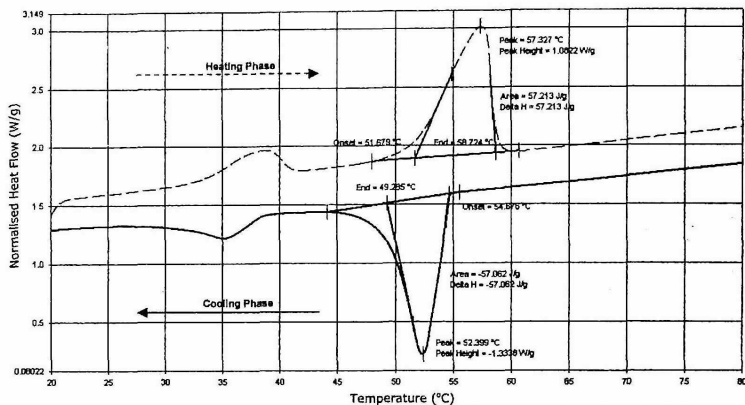


Figure 6: Thermograph of a 30% Concentration Paraffin Composite MicroPCM Slurry

Figure 6, illustrates the thermograph for a 30% concentration of the paraffin composite with water. It showed particularly good thermal characteristics with a latent heat of fusion of 57.2 J/g at this concentration. At 100%, this was measured at 189 J/g. The range of phase transition and the temperature range between melt and solidification was the factor that made this PCM stand out over the other materials. It exhibited little supercooling and had a phase transitional temperature of 55°C. All phase change was likely to occur within the temperature limits of the fuel cell system.

3.6.3 Capsule Strength

Thermal Gravimetric Analysis (TGA) is a measurement of the mass of a sample as a function of temperature. And was used in this study as an indication of capsule durability. The microPCM was heated and the decomposition curves recorded.

Figure 7, illustrates TGA curves for some of the microPCMs under investigation. Previously tested microPCM of n-eicosane were evaluated in a pumped circuit with over 20,000 cycles of operation and showed no significant signs of degradation. This was

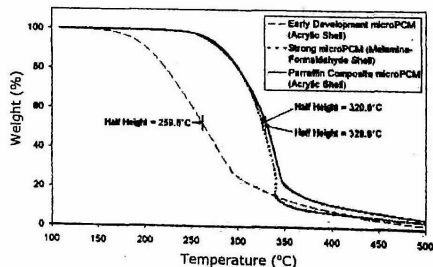


Figure 7: Thermal Gravimetric Analysis

tested with TGA (half height, 320°C) and provided a target for the development microPCM. Early encapsulation techniques showed poor durability with reduced half heights at ~260°C. This was improved to 330°C for the final paraffin composite.

CONCLUSIONS

This paper presents the development of a new microPCM designed to operate in a fuel cell thermal system. The development work has created a microPCM that shows very favourable and tuned characteristics to the fuel cell operating conditions. Further investigation is necessary to quantify reductions in pumping loads and improvements in heat transfer.

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