DEVELOPMENT OF HIGH PERFORMANCE SCALED-UP PEMFC USING POROUS INSERTS INCORPORATED SERPENTINE FLOW FIELD

A SYNOPSIS

Submitted by

KARTHIKEYAN M

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FACULTY OF MECHANICAL ENGINEERING

ANNA UNIVERSITY

CHENNAI 600 025

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1 INTRODUCTION

Fuel cell is an electrochemical device that directly converts chemical energy of fuel and oxidant into electrical energy with only water and heat as byproducts due to oxidation reaction on anode and reduction reaction on cathode takes place. PEMFC which uses hydrogen as fuel due to its high energy density and its optimum operating pressure, temperature, quicker startup and environmental friendliness makes it one of the promising alternative power generation source for automobile applications. The main component of fuel cell is Membrane Electrode Assembly (MEA) which is combination of membrane, catalysts and Gas Diffusion Layer (GDL), flow plates containing flow channels, current collectors and end plates. Even though the PEMFCs have many advantages like higher efficiency, simple construction and versatility, commercialization of fuel cells is inhibited by its drawbacks such as high cost due to use of noble metals such as platinum as catalysts, water management issues while scaling up and thermal management issues while stacking up [Tsutomu Ioroi *et al.* (2018)]. The incremental reduction in cost of the fuel cell will result in significant reduction in cost while fabricating fuel cell stacks. Addressing the above issues in the development of high energy density PEMFC system will make a pathway to commercialization of PEMFCs for automotive and power generating applications.

Experimental studies [Karthikeyan *et al.* (2014)] in scaling up of fuel cell resulted in 40% drop in fuel cell performance while increasing the active area of fuel cell. In case of smaller fuel cells, the water produced is carried away by the flow of reactants. However, while scaling up, water lodging at GDL starts to become significant. It is important that the water content should be optimum. Too low water content will reduce PEMFC performance due to membrane dehydration [Hui *et al.* (2008)]. Too high water content hinders proton transfer thus reducing electrochemical reactions and PEMFC performance [Mench (2008)]. Flow channel geometry [Owejan *et al.* (2007)] plays an important role in water management. Serpentine flow field produces better performance among various flow field designs such as parallel, interdigitated, integrated, straight, pin type and annular, etc [Manso *et al.* (2012)]. Use of integrated electroosmotic pumping acts as an active method of water removal [Buie *et al.* (2006)]. Karthikeyan *et al.* (2012) experimentally compared the performance of conventional serpentine flow field and porous serpentine flow field using resin-bonded sheets of carbon. The porous nature of the flow field combined with carbon used as base material provided the flow field with high porosity, better electrical conductivity and high gas permeability. The high porosity of the flow field impacted the water accumulation at GDL and flow channel. This produced a higher power density compared to conventional serpentine flow field. However, the performance of the fuel cell dropped at ohmic and concentration regions due to cross flow of reactants in fuel cell from flow channels through rib surfaces. Also, machining and handling of porous flow fields were challenging tasks due to their brittle nature. This prompts for design of conventional flow fields with porous inserts along the rib surface of the flow channel. Experimental investigations [Karthikeyan *et al.* (2015)] has proven that use of porous inserts in grooves machined on conventional flow channel increases the performance of fuel cells by effectively removing the excess water from the flow channel through porous inserts by means of capillary effect. From the literature, a gap in studying scaling up of fuel cells is identified which can be bridged through increasing the size of porous inserts, proper positioning of porous inserts along the rib surface of the flow channel, optimising the porosity and choosing optimum material for porous inserts for better water management while scaling the the fuel cells.

2 OBJECTIVES

The main objective of this work is to

- Experimentally study the effect of Porous inserts (carbon inserts and sponge inserts), their porosity (70%, 80% and 90%) and their size (2 mm and 4 mm) on performance of PEMFC with following flow channels in anode and cathode respectively.
    - Serpentine – Serpentine
    - Serpentine – Modified serpentine flow field with inline arrangement of porous inserts (MSI)
    - Serpentine – Modified serpentine flow field with staggered arrangement of porous inserts (MSS)
- Analyse scaled up best performing flow field to various active areas of PEMFC and compare the same with serpentine flow field.

This work endeavours to overcome the gap identified in literature by using different materials for porous inserts, varying the porosity and increasing the size of the porous inserts for enhanced performance of PEMFC.

3 METHODOLOGY

- This work experimentally analyses the performance of PEMFC with active areas of 25 cm^2, 36 cm^2 and 70 cm^2 with serpentine flow channel on both anode and cathode side.

- Porous carbon inserts of three different porosities namely 70%, 80% and 90% were fixed along the rib surface of the flow channel. Porosity with highest water removal rate is used for further studies.

- Increasing the size of Porous carbon inserts (PCI)- MSI with 2 mm PCI, MSI with 4 mm PCI, MSS with 2 mm PCI and MSS with 4 mm PCI were studied for better water management.

- Further investigation on the Performance of PEMFC has been carried out by using Porous sponge inserts (PSI) for MSS with 2 mm and 4 mm for better water management.

- The optimized size, material and porosity of the porous insert is used in best performing flow field for various active area of PEMFC.

The workflow in this study is given Figure 1.

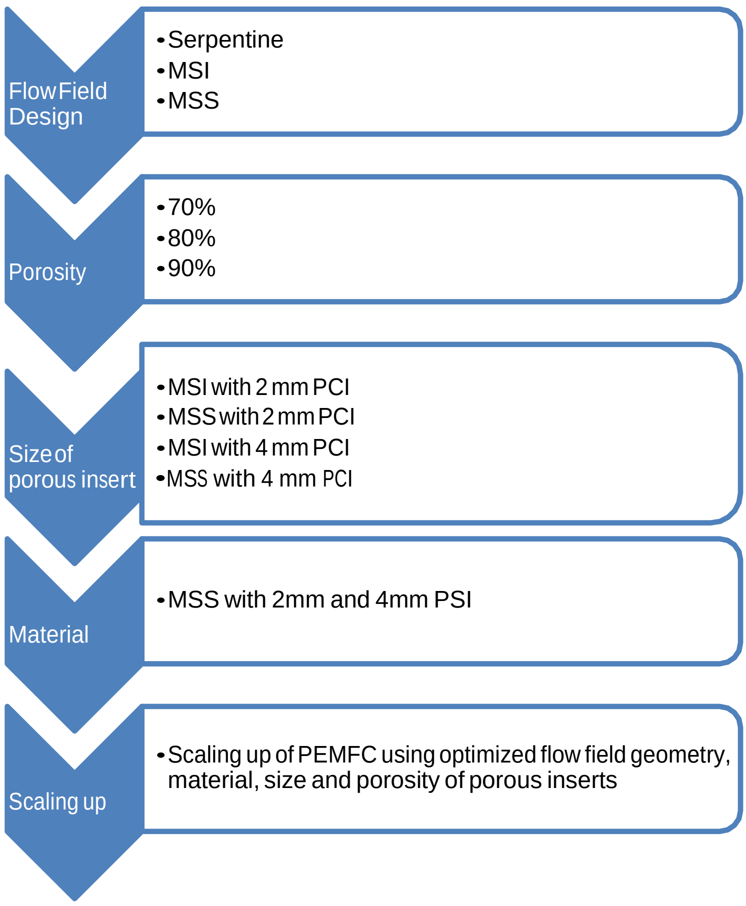

Figure 1 Workflow

4 DESIGN CONFIGURATION OF FLOW CHANNELS

Based on the literature, it is found that the performance of serpentine flow channel is higher due to better water transportation properties. Hence, serpentine flow field is used in anode side of all the experiments. However, during scaling up of fuel cells, water management is poor due to longer flow paths. In addition, increasing active area further increases the water formed in the cell due to more electrochemical reactions. So, effective water control is required with the novel flow field while scaling up PEMFC. Thus, two novel modifications are introduced in the serpentine flow field by modifying it to accommodate porous inserts in inline and staggered arrangements for increasing the rate of water removal in cathode side since accumulation of water in cathode side more due to oxygen reduction reaction resulting in water formation. A landing to channel width of 2 mm to 2 mm is considered for all the experiments for easier machining and accommodation of porous inserts even though this configuration has a slightly less performance compared to flow channels having 1 mm to 1 mm landing to channel.

5 OVERVIEW OF CHAPTERS

Chapter 1 discusses the basics of fuel cell, suitability of PEMFC for automotive applications, merits and demerits of PEMFC, scaling up of fuel cells, water management issues, impact of flow field geometry, use of complete porous flow field along with its advantages and disadvantages, need for incorporation of porous inserts along with appropriate literature. The concerns that are addressed in this work such as porosity, size and material of porous inserts along with different flow fields are also discussed.

Chapter 2 reviews various literature regarding (i) scaling up studies, (ii) water management issues, (iii) flow field modification and (iv) material selection along with latest advances in fuel cell research. The knowledge gap identification on the literature studies, objective and methodology of this work which includes investigation of the effect of material, porosity, size of porous inserts in various flow field designs such as serpentine, MSI and MSS flow fields. It also addresses the scaling up of PEMFC.

Chapter 3 describes the selection of active areas, modification of flow field design, scientific evaluation of porous insert technology, selection of materials for porous inserts, preparation of porous inserts, positioning the porous inserts on the rib surface of the flow channel.

The porous carbon inserts are the small cubical/cuboidal solid substances/bodies made of Vulcan carbon, which have the properties of good water absorption through their high porous structure along with good electrical and heat conductivities. Porous carbon inserts are prepared by using Vulcan carbon as base material and PolyVinyl Alcohol (PVA) as binder material. Initially, a polymer solution is prepared by dissolving 0.3 g of PVA in 30 ml of distilled water with a magnetic stirrer. The polymer solution is then added dropwise to the Vulcan carbon until the mixture reaches a semisolid state. The mixture is then cast into cubical/cuboidal inserts. The casted carbon inserts are then sintered at 300^{o}C in a furnace for vaporizing the binding polymer PVA. Also, this sintering process improves the structural strength and porosity of the porous inserts by the removal of polymer binder.

The porous sponge inserts are prepared by converting phenolic foam into carbon foam by means of pyrolysis. This is achieved by heating phenolic foam in an inert hydrogen atmosphere from room temperature to 1000 ^{o}C at 100 ^{o}C/hr rate to effect the conversion. Then, the carbon foam is cut into porous sponge inserts of required sizes.

The porosity of porous inserts is found by Liquid absorption method which utilizes a non-reactive liquid such as glycerol to fill up the pores. The difference of initial and final weights of the porous inserts before and after dipping into the glycerol gives the weight of glycerol entered into the pores of the carbon insert. The porosity (P%) can be measured from the change in weight (Δw) of porous inserts, the density of glycerol (ρ = 1.261 g/cm^3) and volume of porous inserts (8 mm^3), by using equation (1).

$$P\% = \frac{\Delta w}{\rho} X \frac{1}{Volume} X\ 100\% \qquad (1)$$

The porous inserts are placed in the grooves with the help of tweezers in the landings of MSI and MSS flow fields by using a thin layer of electrically conductive glue which is applied on the bottom face of the porous insert to ensure that they are fixed firmly. The porous inserts will block the passage of the oxygen flow in the cathode flow channel if they fall off from their corresponding positions. The positioning of porous inserts along the grooves of flow field changes the flow field design from pin type to modified serpentine type which is essential for improved water management on cathode side of PEMFC.

Chapter 4 elaborates the details of the test station used for testing the fuel cell, MEA preparation, parameters maintained while hot pressing, the techniques used to activate the Nafion membrane in order to increase its proton conductivity by rehydration, operating conditions during experiment and characteristics studied during testing to measure performance of the fuel cell.

The MEA is prepared by sandwiching commercially available Nafion polymer membrane between two Gas Diffusion Electrodes (GDE).The Nafion membrane has a thickness of 183 µm and acts as a barrier between cathode compartment carrying oxygen and anode compartment carrying hydrogen. The Nafion polymer membrane is a solid electrolyte which allows only protons of hydrogen to pass through it. The GDE holds platinum-based catalyst with 20% Pt on carbon with a loading 0.5 $mgPt/cm^2$ along with carbon paper which allows the reactants to pass through by means of diffusion. The Nafion polymer membrane is initially cut to 8 cm X 8 cm and treated with 5% solution of hydrogen peroxide and 0.5 molar solution of sulphuric acid alternatively for 1 hour each and treated with water at later stages to remove any traces of chemicals.

Now, the 8 cm X 8 cm membrane is sandwiched between GDEs of 5 cm X 5 cm on each side at a temperature of 140 ^{o}C and a pressure of 50 kg/cm^2 for a period 3 minutes.

Initially, activation is required for properly humidifying the MEA which might be dried out during the hot pressing in the fabrication of the 5 layer MEA. The anode GDL and catalyst layers, membrane, cathode catalyst layer and GDL are the five layers of MEA. The following procedure is developed for activation of MEA based on a number of trials which include constant power, constant current and constant voltage modes by using a looping process. Primarily, a Voltage pulse with 0.6 V constant voltage is maintained for one hour, followed by a looping process, which alternates between 0.7 V and 0.5 V for every 20 minutes until the value of current produced reaches a maximum for the given voltage. Finally, a current pulse with a current density of 200 mA/cm^2 is maintained until the stabilization of voltage takes place for all PEMFCs. The activation of MEA guarantees that the MEA can perform at its maximum power density by activating catalyst sites during this process. The studies on scaling up of fuel cells are continued after the activation of MEA.

The Biologic FCT-50Sis a computer integrated test station, which is programmed to control the load, pressure, temperature, relative humidity and flow rate of reactants accurately. The data acquisition is attained by use of an Ethernet cable. The fuel cell test station can be used to measure up to 250 W power with current and voltage up to a maximum of 50 A and 5 V respectively. Flow rate of reactant up to 1.5 lpm on anode side and 1.0 lpm on cathode side with a stoichiometric ratio of 2 can be maintained for all experimental studies. Hydrogen of 99.99% purity is used as fuel on anode side and medical grade oxygen is used as oxidant on cathode side. Pressure gauges which are in line with the outlet of the reactants are used to measure the pressure in the fuel cell.

'Voltage pulse' and 'Current scan' experiments have been performed among various experiments available in the test station. The voltage pulse steps the potential with reference to absolute potential (E) or initial potential. This is based on the estimated current response for potential step applied. The current scan sweeps the applied current to the PEMFC from zero in programmed increments until a set value is finally reached. This gives an estimate of the maximum power density and voltages of the PEMFC.

Chapter 5 explains the effect of porosity, position, material and size of porous inserts on the performance of 25cm^2 PEMFC.

The power densities obtained from three flow fields [Figure 2(a)], namely serpentine, MSI with PCI and MSS with PCI are 0.242 W/cm^2, 0.265 W/cm^2 and 0.27 W/cm^2 respectively for an active area of 25 cm^2. The performance of the PEMFC fixed with porous inserts are influenced by the capillary effect of PCI which aids in effective water removal which in turn eliminates the stagnation water under the landing diminishing the effect of water flooding at the interfacial region between the GDL and landing area. After reaching the maximum water retention capacity after absorbing the water at GDL-landing area interface, the PCI begins to drain out excess water to adjacent flow channel located below the rib. This water is forced by the force of the reactant stream to flow channel outlet.

While comparing porous inserts of different porosities shown in Figure 2(b) namely 70%, 80% and 90%, the PEMFCs with MSS flow field produced peak power densities of 0.247 W/cm^2, 0.261 W/cm^2 and 0.27 W/cm^2 respectively. There is slight increase in performance of PEMFC with increase in porosity. This is because of improved water transport properties that accompany with increase in porosity.

Analysing flow fields with different sizes of porous inserts [Fig. 2(c)], the flow fields namely MSI with 2 mm PCI, MSI with 4 mm PCI, MSS with 2 mm PCI and MSS with 4 mm PCI produced 0.265 W/cm^2, 0.319 W/cm^2, 0.270 W/cm^2 and 0.345 W/cm^2 respectively. The modified flow field shows better performance because the fixation of porous inserts on the flow field converts it into serpentine flow field inheriting the better water transportation property of serpentine flow field along with water absorbing property of flow channel.

The MSS with PCI has better water management compared to MSI with PCI and serpentine flow field. In MSI flow field, the porous inserts follows an order of uniformity. However, in MSS flow field, the porous inserts do not follow any uniformity with its adjacent landing surface. As a result, in the MSS flow field, the water absorption becomes more globalized and the majority of the area gets covered for water absorption, but in MSI flow field, the localized water absorption is seen. So the performance of MSS flow field is better than MSI flow field. The PCI's volume doubles when its size is increased from 2 mm to 4 mm which in turn increases the absorption and retention of water. Since, more water is absorbed and retained, the lodging of water is considerably reduced which in turn increases the performance of PEMFC.

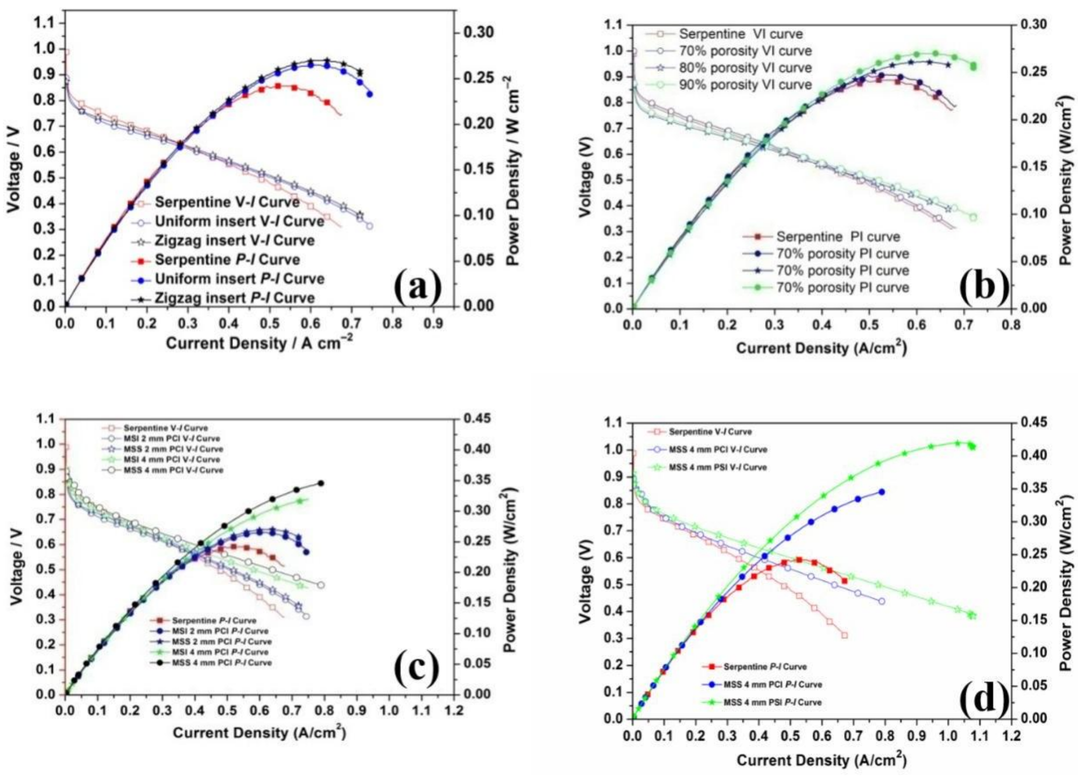

Figure 2 Polarisation (VI) and Performance (PI) for (a) Serpentine, MSI with PCI and MSS with PCI flow fields (b) Porous inserts of porosity 70%, 80% and 90% (c) Serpentine, MSI with 2 mm PCI, MSI with 4 mm PCI, MSS with 2 mm PCI and MSS with 4 mm PCI flow fields and (d) Serpentine, MSS with 4 mm PCI and MSS with 4 mm PSI flow fields.

However, on a prolonged run the PCI showed less durability by dissolving in the water. To overcome this issue, a new porous material porous carbon sponge (PSI) used instead PCI.

Studying the effect of material of porous inserts shown in Fig. 2(d), the flow fields namely MSS with 4 mm PCI and MSS with 4 mm PSI produced 0.345 W/cm^2 and 0.42 W/cm^2 power densities respectively. This shows that using porous sponge insert instead of porous carbon insert increases the power density of the PEMFC. This may be due to the better water absorption property of sponge.

Chapter 6 elaborates scaling up of fuel cell active area using MSS flow field with 4 mm PSI based on the experimental results on 25cm^2 PEMFC and comparison with serpentine flow field of respective sizes.

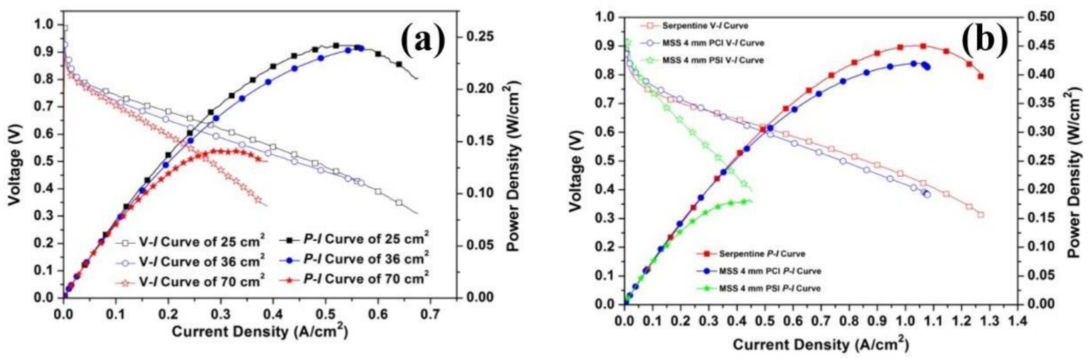

Figure 3 Polarisation (VI) and Performance (PI) for 25 cm^2, 36 cm^2 and 70 cm^2 active areas for(a) Serpentine flow field (b) MSS with 4 mm PSI flow fields.

Initial studies on scaling up of active area of PEMFC from 25 cm^2 to 36 cm^{2}and 70 cm^2 using serpentine flow field [Fig. 3(a)] yielded power densities of 0.242 W/cm^2, 0.24 W/cm^2 and 0.171 W/cm^2. The scaling up process reduces PEMFC performance due to water flooding in flow channels. This is because flow path length in 25 cm^2 is comparatively shorter than flow path length in 36 cm^2 and 70 cm^2. So water removal is easier. But water removal becomes difficult while increasing active area of PEMFC.

While using MSS with PSI of 4 mm in 25 cm^2, 36 cm^2 and 70 cm^2 PEMFCs , the power densities obtained were 0.42 W/cm^2, 0.451 W/cm^2 and 0.182 W/cm^2 respectively [Figure 3(b)].

Flow field design	Active Area		
	25 cm^2 PEMFC	**36 cm^2 PEMFC**	**70 cm^2 PEMFC**
Serpentine flow field Peak Power density (W/cm^2)	0.242	0.24	0.141
% increase in power density due to scaling up compared to 25 cm^2 active area (Serpentine)	-	-0.82	-41.74
MSS flow field with 4 mm PSI Peak Power density (W/cm^2)	0.42	0.451	0.182
% increase in power density due to scaling up compared to 25 cm^2 active area (MSS with 4 mm PSI)	-	25.18	-37.04
% increase in power density due to use of optimized flow field with PSI compared to serpentine flow channel	73.55	87.91	29.07

Chapter 7 summarizes the conclusion and scope for future work. The major points in conclusion are,

Among three active areas of PEMFC used with serpentine flow field, the maximum performance is obtained from 25 cm^2 active area and minimum performance from 70 cm^2 active area.

MSS with 2 mm PCI yields high power density compared to MSI with 2 mm PCI and serpentine flow field.

Porous inserts with 90% porosity achieved highest power density among porosities of 70%, 80% and 90%.

Comparing five different flow fields namely serpentine, MSI with 2 mm PCI, MSI with 4 mm PCI, MSS with 2 PSI and MSS with 4 mm PSI, the highest power density was achieved by MSS with 4 mm PSI in an active area of 25 cm^2.

The novel MSS flow field with 4 mm PSI shows 73.55%, 87.91% and 29.07% increase in power densities for 25 cm^2 to 36 cm^2 and 70 cm^2 compared to serpentine flow fields of same sizes.

Flow channels with hydrophobic coating along with porous inserts could be analyzed in future to further enhance water removal.

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LIST OF PUBLICATIONS

International Journal

1. **Karthikeyan, M,** Muthukumar, M, Karthikeyan, P & Mathan, C 2019, ‘Optimization of Active Area of Proton Exchange Membrane Fuel Cell with Better Water Management’, Journal of Ceramic Processing Research, vol. 20, pp.1-9, ISSN: 1229-9162, **Impact Factor- 0.386** (Sl.No. 5762).