

Use of Mercury Intrusion Porosimetry (MIP) Technique to Measure the Porosity of Anodes in Solid Oxide Fuel Cell (SOFC)

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Abstract

The present research is aimed to calculating the porosity of anodes in solid oxide fuel cell through Mercury Intrusion porosimetry (MIP). There are various techniques used to measure the porosity of the solid oxide fuel cell (SOFC). MIP is a method used to find the porosity of anodes due to its high accuracy, and some additional information which includes particle size distribution, pore size distribution, average pore size and bulk density. The working principal of MIP is that when sample is filled with mercury then high pressure is applied which makes the mercury to penetrate into the pores of the sample. The instrument measures the pore volume with the help of capacitive system as the pressure gradually increases to its maximum value and then decrease to its lowest value. This system calculates the volume of mercury intruded for each pressure whether the pressure is increasing or decreasing. The instrument is connected to a computer with dedicated software which calculates the percentage porosity of the sample. The results suggested the importance of PH and agitator on porosity. What we have to provide is the sample mass, sample density and the temperature of the laboratory. However for cleaning purposes of mercury, ethanol could be used instead of acetone, as mercury intrusion porosimeter involves few plastic parts like dilatometer holder and cap. Whereas acetone has catastrophic effect on them, and these parts are very expensive to replace.

Keywords: Mercury, Intrusion, Solid oxide, Fuel cell, Porosity, Anodes, Porosimetry

1. Introduction

There are many ways through which we can measure porosity of a sample; following are some of the important porosity measurement techniques which are commonly used in the material laboratory. In this study only mercury intrusion methods and results are discussed.

1.1 Image analysis

This is the simplest of the technique in measuring the porosity. In this technique properly sectioned, mounted and polished sample is put under the microscope, normally optical microscope or scanning electron microscope (SEM). SEM is preferred because of its very high magnification .image is obtained from the microscope in the digital form and is further analysed by different image analysis software like image pro plus [1][2][3]. These software's carries out different image enhancement steps like contrast adjustment, brightness adjustment, and non-uniform illumination correction in order to bring out the distinct phases, then the software calculates the area fraction of each phase by counting the number of pixels in each phase. Pores in the image are show as separate phases so there area is also calculated and by dividing the pore area by the total area percent porosity of the sample is calculated [4]. Another variation of image analysis is manual point counting method in which a section of the image is selected and grid is placed over the image and area of each phase is calculated. [34] The biggest advantage of the image analysis is that it allows to measure both the open and closed porosity .while the drawback as mentioned by (Karn and Allen,2004) are it damages the sample ,requires specialized equipment and the porosity of the sample is assumed to be the representative of the whole sample [5].

1.2 Water Archimedean Method (WAM) Porosimetry (AP)

Also known as water immersion or water impregnation or water Archimedean porosimetry. This method is the most simple and straight forward one, which gives us the open porosity and Skelton density and is a non-destructive technique. This method is based on the basic principal that when the sample is immersed in water it gains weight; this gain in weight is equal to the volume of the pores.

In AR method sample is first weighed dry in air(G_0) ,then sample is soaked in water for some time and weighed(G_1) by suspending it in distilled water through very thin wire again the saturated sample with water is weighed(G_2) in air .Percent Porosity is calculated using the formula

$$P = (G_2 - G_0) \times 100 / (G_2 - G_1)$$

Similarly skeleton density is determined by the formula

$$\rho = G_0 / G_2 - G_1$$

If the water used is not distilled water or any other solvent is used then we have to multiply both the equations by density of that medium [6].

Although the general principal remains the same but lot of procedural variations are cited in the literature in order to ensure the through impregnation of water in to the pores.

(Kerry and Johnson, 2006) mentioned by placing the dry sample under vacuum chamber for 30 min, then introduce the water in the pressurised chamber for 60 min and then take the weights G2 and G1 .Another technique they mentioned is to immerse the sample in boiling water for at least two hours for coarse grained samples, and for at least five hours for fine grained samples [7]

Similarly (Murakami, 1998) mentioned three techniques for best immersion of water in to the pores. In the first technique, the ASTM Standard Test Method (C373-72) was adopted, in which the deposits were boiled in distilled water for 5 hours, followed by soaking for an additional 1 day. The second method is referred to as a "modified ASTM method" where the deposits were held for 600s in a desiccators at a pressure of 3.3 kPa above the deaerated distilled water at ambient temperature, then, the deposits were boiled for 5 hours at atmospheric pressure, followed by soaking for an additional 1 day. In the third method, the deposits were immersed in distilled water at 291 K at atmospheric pressure, and then the porosity was measured every day by weighing the deposits in water and in air [8].

Despite being the most common method for porosity measurement water immersion porosimetry has its down sides .first of all it assumes that all the water has penetrated in to the pores while the actual fact is that it is very difficult to penetrate water in to very small pores, thus giving wrong results .blotting is a major source of error in this method, because when sample is blotted a bit hard it can bring out the water from the pores which can give variable results. Also there is a possibility of rehydration when samples are boiled in hot water, thus giving wrong results [9].

1.3 Mercury intrusion porosimetry (MIP)

This method is highly automatic therefore more accurate and precise compared to other techniques. In this method an evacuated sample is filled with mercury at a steady rate of increasing pressure [10]. Mercury penetrates in to the pores of the sample with increasing pressure .larger pores gets filled with mercury at lower pressure and vice versa .the data is obtained in the form of pressure volume graph .this data is used to calculate the pore size using Washburn equation assuming all the pores are of cylindrical shape .

$$d = -4\gamma\cos\theta/P$$

Where

d = diameter of the intruded pore,

γ = surface tension of mercury,

θ = contact angle between mercury and the pore wall

And

p = applied pressure.

MIP can measure pore diameter from few nanometre to hundreds of micron meter depending on how much pressure is applied .currently there are porosimeter available whose maximum pressure is as high as 400 MPa which can force mercury even in to the tinniest of the pores .porosity of the sample is determined using the formula

$$\Phi_0 = (\rho_s - \rho_b/\rho_s)\times 100 \%$$

ρ_b is bulk density calculated by dividing specimen mass over specimen volume at zero pressure and skeletal density ρ_s is Skelton density calculated by dividing the specimen mass over specimen volume at maximum pressure, with the open pores filled with mercury [11].

MIP has also got its limitations .it is a destructive technique, samples once used in it cannot be reused because it's very difficult to remove all the mercury from the pores .also it only measure those pores which are connected to the surface thus gives no idea about closed porosity .pore size distribution should also be taken only in the semi quantitative way because MIP considers all pores as cylindrical. Also, the so-called 'bottleneck effect' has to be considered , the volume of a larger pore, connected to the surface through a smaller opening, is intruded only at a pressure corresponding to the smaller diameter[12][13].

1.4 Helium Pycnometry

Although this method does not give porosity independently but can be used in combination with AP and MIP for accurate results .The biggest advantage of this method is that beside open porosity it also gives values for closed porosity because of the fact that helium is the second most lightest element in periodic table ,so because of its smaller size it can penetrate almost anywhere .In this method the sample is weighed and placed on a pycnometer of known volume .the pycnometer is then filled with Helium gas at constant pressure .Helium penetrates in to the pores of the samples and difference in volume of filled and unfilled state is measured which

gives the specimen volume, which is used to calculate the specific density. This specific density is used in collaboration with MIP and WAM to calculate the total porosity [14].

$$\Phi_t = (\rho_s - \rho_b/\rho_s) \times 100$$

Where ρ_s is used to determine ρ_s the skeletal density, and MIP or AP is used to determine ρ_b is the bulk density. Closed porosity is then calculated by subtracting the open porosity from total porosity where MIP and AP give the values for open porosity.

$$\Phi_c = \Phi_t - \Phi_o$$

1.5 Columetric method

Columetric method is another technique mentioned by (Celis, drees, Maesen and Roos, 1992) for the determination of porosity in thin ceramic coating. In this method porosity of the coating is determined from the anodic polarization of substrate and coated sample. As both materials undergoes oxidation to a different extent and according to Faraday's law the amount of electrical charge produced is proportional to the total amount of material been oxidized. From the above assumptions a formula was devised to measure Percentage porosity as given below.

$$\Phi = (Q_{cs} - Q_{cm}/Q_s) \times 100$$

Where Q_{cs} is the amount of charge measured through coated sample, Q_s is the amount of charge measured through substrate, and Q_{cm} is factor given for the dissolution of the coating in the electrolytic solution [15][16].

1.6 BET Surface area and pore size analysis

BET Surface area analyser works more or less on the same lines as mercury intrusion porosimetry, but because intruding medium is gas so surface area analyser can measure porosity of micro and meso level while MIP measures pore volume of meso and macro level. Here it should be noted that no single technique is available which can measure porosity of all pore size ranges.

Table 1. Classifications of Pore size distribution [17]

| Classification | Pore diameter range (nm) | Pore diameter range (μm) | Pore diameter range (\AA) |
|----------------|--------------------------|---------------------------------------|--------------------------------------|
| Micro pores | < 2.0 | < 0.002 | < 20 |
| Mesopores | 2 – 50 | 0.002 – 0.05 | 20 – 500 |
| Macro pores | > 50 | > 0.05 | > 500 |

In BET (Brunauer, Emmett, and Teller) technique the porosity of the solid sample is calculated from the surface area analysis using bet equation.

In this technique a gas is made to flow in two tubes one tube contains the sample while the other is empty. Both these tubes are in absolute identical conditions. Now these tubes are immersed in liquid nitrogen bath in order to maintain a constant temperature and highly pure nitrogen gas is introduced in both the tube at same pressure. The pressure in the sample tube decrease because of the absorption of the gas by the sample. This system automatically notes the difference in pressure. A servo valve brings the pressure at par with the reference tube by introducing more gas in the sample tube the varying rate of gas delivery is then used in BET equation (either single or multilayer) to calculate the surface area, pore size and pore size distribution [18]. X-Ray diffraction, μCT and synchrotron X-ray micro Computer Tomography and Impedance balance are also sometimes used to measure porosity [19].

2. Material & Methods

2.1 Mercury intrusion Porosimetry (MIP)

MIP is a method used to find the porosity of anodes because of its high accuracy, and some extra information which it gives about particle size distribution, pore size distribution, average pore size and bulk density. Instrument used are PASCAL-140 and PASCAL 240 from Thermo Quest instruments, and highly pure Treble distilled mercury is used. Three stages are involved to measure the porosity of coating through MIP.

2.1.2 Stage 1

Before the actual analysis of sample is carried out a blank analysis to run. Blank is run to remove all the values of decrease in mercury volume, which are not because of intrusion in to the sample pores. This includes the mercury going into the pores of the glass dilatometer and the effect of mercury compressibility at high pressure, which otherwise will be interpreted as volume going in to pores. Blank follows all the steps for the actual sample analysis. The only difference is that blank don't contains any sample. Once blank reading is obtained it is regularly subtracted from the reading of the sample.

2.1.2 Stage 2

Second stage is running the analysis of the alumina tile. Blank reading is subtracted from the alumina. The result of alumina taken from instrument is given in appendix 8(a). Once the result of alumina is obtained it is

subtracted manually from the result of each sample.

2.1.3 Stage 3

Blank and alumina are run only once. In stage 3 all the samples are run. Result of sample is given in the results and discussions.

2.2 Functioning of the instrument

The working principal of MIP is that when sample is filled with mercury high pressure is applied which makes the mercury to penetrate in the pores of the sample. The instrument measures the pore volume with the help of capacitive system .as the pressure gradually increases to its maximum value and then decrease to its lowest value, that system calculates the volume of mercury intruded for each pressure both when pressure is increasing and decreasing . The instrument is connected to computer with dedicated software which calculates the Percentage porosity of the sample .only we have to provide the sample mass, sample density and the temperature of the laboratory.

The operation of instrument involves outgassing the dilatometer, in outgassing the pressure comes down to 0.01KPa, where dilatometer is a glass tube which holds the sample, and has a characteristic number on it which tells us the maximum volume it can hold and also the size and type of sample used e.g. powder or solid . In the experiments CD3 type dilatometer is used. Once outgassing is done then the dilatometer is filled with mercury. Filled volume of the mercury is noted. Then pressure is applied, which increases to its maximum value, and then comes back to vacuum. Volume difference of mercury at each pressure both increasing and decreasing is automatically calculated by the instrument.

Initially PASCAL -140 porosimeter was selected which has a maximum pressure of 400kpa, but when the blank analysis is carried out it gave zero reading. It was repeated three times but with same result. Even when sample is run it gave very low value, the reason was that the pressure in PASCAL- 140 was not high enough to make mercury penetrate in to small pores. So it is decided that PASCAL 240 also used in collaboration with PASCAL- 140, because PASCAL-140 can only detect macro and ultra-macro pores, while PASCAL 240 can detect meso-pores as well because of high pressure up to 200MPa.

2.3 Problems faced in operation of Mercury intrusion Porosimeter

Problem 1 – Achieving 0.01 kpa during the out gassing stage of Pascal 140 has been difficult with the pressure always stopping between 0.02 to 0.07kpa. If eventually 0.01 kpa is achieved and the filling stage activated, the result has been an error message WARNING FILLING EXCESS, a scenario that also plays out if it is attempted to fill mercury before achieving 0.01kpa.

Problem 2 – On some occasions after getting reasonable mercury fills such as 448mm³ on the CD3, during the analytical run, the machines measurement of volume goes as high as 556mm³, while dilatometer can only hold volume of 500mm³.

Problem 3 –some times, even when the PASCAL-140 machine is displaying excess fill, the bulb of the dilatometer is only half full.

Problem 4 – it also happened that when it is attempted to outgas on the PASCAL-140, but after a lengthy period of time it simply gave a message – Outgas time too long

Problem 5–On one occasion even when all the above problems are removed, when the dilatometer is evacuated the pressure was not going down to 0.01kpa. It was tried ten twelve times but on each occasion it stops at 0.08 or 0.07Kpa.

Problem 6–on one occasion after successful outgassing, filling and running the sample on the PASCAL 140, when high pressure on PASCAL -240 is applied it gave the error message of Piston over limit. It is repeated three times but with the same result.

Problem 7–On two occasions stem of the dilatometer break away, once I tried to pull the stem out of the dilatometer ,and other time I inserted a pin to press the mercury down, so that stem can be separated from dilatometer.

3. Results and Discussions

On investigation it was revealed that problem 1, 2 and problem 3 are because of the contaminated dilatometer holder, as the holder is made of plastic and has got in touch with acetone which has catastrophic effect on plastics while problem 4 was because of dirty seal between dilatometer and the Mercury head. When seal is cleaned and made sure that the dilatometer is seated correctly at the right place before out gassing, that problem sorted out.

However the problem 5 is due to the dilatometer is used in Pascal 240 which also uses some dielectric oil, that dielectric oil got stuck in the stem of the dilatometer which is not removed by acetone. So when stem is cleaned with soap it worked and pressure did come down to 0.01Kpa. Problem 6 is because waste valve of autoclave of PASCAL-240 remained open because of defective screw .which is then tightened by plier.

Whereas in problem 7 in first incidence fatigue may be a possible reason for breaking of the stem, because dilatometer and stem are opened by pulling, and because of that pulling fatigue is developed in the stem which eventually caused the breaking. While in second incident, when a specially designed pin with rubber tip is inserted in the stem it caused the chipping of the stem. Normally that pin moves in the stem very easily but on that occasion it stuck up. On careful observation it revealed that the rubber on the tip of the pin has swollen up because of getting in contact with acetone.

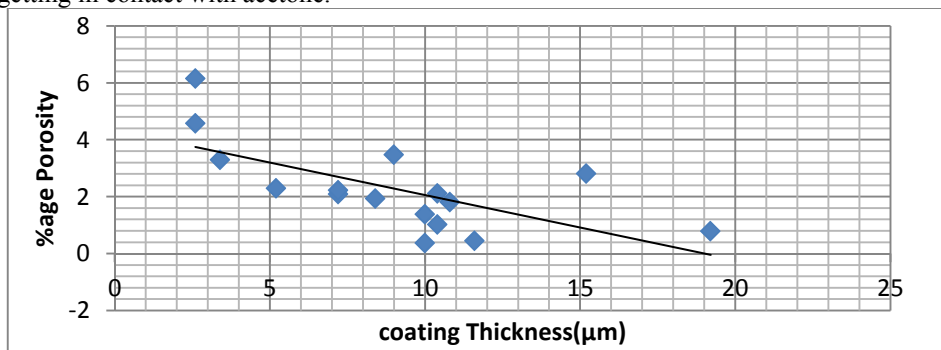


Fig 1 graph thickness vs. percentage porosity

3.1 Cleaning and handling of mercury

Mercury is a toxic metal, and extreme care is taken while handling mercury. Masks and gloves are worn all the time while handling mercury. Even very small amount of Mercury has tendency to make fumes at room temperature because of its very high vapour pressure. Continuous exposure to these fumes can cause skin and kidney problems. All the metallic objects are removed because mercury has a tendency to form amalgam with metals especially with gold and silver. Dilatometer is thoroughly cleaned from mercury using acetone. While opening the filled dilatometer, care is taken to avoid any spillage. Because when mercury spills it disintegrate in to tiny droplets which are difficult to collect. Once all the mercury is removed, dilatometer and stem are washed with soap because in PASCAL 240 dielectric oil is used and acetone is not good enough to remove all the oil from stem. After washing dilatometer it is dried until all the water and acetone has evaporated. It is always advisable to give some extra time for drying, because even if small amount of impurity is left vacuum can't be achieved, which is first requirement of MIP. All the samples which are used in MIP are kept in a waste box and discarded properly.

4. Conclusion

The mercury intrusion porosimetry used in conjunction with helium pycnometry would be a good method to calculate total porosity. In return it will give us the values of both open and closed porosity. Furthermore it will help us in establishing a broader view about the mechanical strength and ionic conductivity of the anodes made by this method. In this project four variables in two states are used. The results suggested the importance of PH and agitator on porosity, Therefore it is worthwhile to try more variations of these two variables keeping the other two variables i.e. surface treatment and particle size constant.

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