

Supercapacitor Using a Liquid Dielectric Material

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Abstract- A supercapacitor stores energy electrostatically by polarizing an electrolytic solution. Though it is an electrochemical device there are no chemical reactions involved in its energy storage mechanism. This mechanism is highly reversible, allowing the supercapacitor to be charged and discharged hundreds of thousands to even millions of times. Recent advances in this field have been in developing solid state supercapacitors. In this paper, a low temperature synthesis of PZT by sol-gel route is achieved which is made into a homogeneous solution using Diethylene Glycol. The resulting solution is used as a liquid dielectric in a supercapacitor fabricated using common available plastic containers of different form factors and their electrical properties were measured. The average time taken to charge and discharge the supercapacitor was noted. It was also tested for lowered temperature conditions. The future prospects and applications of this technology are also discussed in this paper.

Index Terms- Supercapacitor, PZT, Ferroelectric materials, sol-gel method, liquid dielectrics.

I. INTRODUCTION

The current research and development efforts on electrochemical power sources are generally focused on fuel cells, batteries and electrochemical capacitors and are directed towards achieving high energy density, high power density and long cycle life at relatively low costs. Yet there is a need for a new class of systems that prevent electrochemical reactions that damage electrodes in normal cells, and avoid a cell balancing requirement in a multicell battery while still providing low manufacturing costs. This has led to a need for reliable electrical energy storage systems.^[3,5,12]

A new technology, the supercapacitor^[5,7], has emerged with the potential to enable major advances in energy storage. Supercapacitors are governed by the same fundamental equations as conventional capacitors, but utilize higher surface area electrodes and thinner dielectrics to achieve greater capacitances. This allows for energy densities greater than those of conventional capacitors and power densities greater than those of batteries. As a result, supercapacitors may become an attractive power solution for an increasing number of applications.

Most research and development done so far in this field is on solid state supercapacitors. In other words, the dielectric used is a solid which is generally made by forming thin films of the dielectric. But this method is found to have certain disadvantages such as

1) Achieving high energy density supercapacitors is not possible without hybrid systems

2) In multicell systems, the cell balancing is required to avoid failure and damage of the cells, in addition to having high reliability.

3) Most of the solid state supercapacitors are based on liquid electrolyte in gel form, coated over thin film supercapacitor material. These systems are normally associated with the well-known disadvantages of corrosion, self-discharge, and low energy density.

4) Attaining high packing density of solid state supercapacitors is always a big task.

In an attempt to eliminate these disadvantages, we make use of a liquid composite dielectric material. The term "liquid composite" refers to a material containing two phases: a dispersed solid phase in a continuous liquid phase. The solid phase is PZT powder which was synthesized using a low temperature sol-gel method. It is dispersed in an organic liquid phase Diethylene Glycol. Ferroelectric lead zirconate titanate ceramics, such as $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT), are largely used in the sensing, actuating and energy storage applications due to their remarkable piezoelectric and dielectric properties^[6,9], and hence was of significant interest for this project.

II. EXPERIMENTAL DETAILS

2.1 Synthesis of LCDM

$\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) was easily synthesized in powder form by an acid based sol gel route^[2] starting from Lead Nitrate ($\text{Pb}(\text{NO}_3)_2$), Zirconium Oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and Titanium (IV) isopropoxide ($\text{TiC}_{12}\text{H}_{28}\text{O}_4$). 1 g of Citric acid was added to 100 ml de-ionized water and stirred for 15 minutes. The aforementioned raw materials, along with 5 ml HNO_3 , are dissolved in this acidic de-ionized water and this solution was stirred for 30 minutes. It was then refluxed for about 2 hours. The refluxed solution was placed in an oven at 100°C for 2 more hours which initiates the gel formation. The obtained precursor was calcined at 600°C for 3 hours and the powder thus formed was grounded. The powder was again heated at slightly higher temperature of 750°C for 3 hours to get the final PZT powders. Figure 1 shows the detailed procedure in a flow chart. Three different batches of powders were made with varying concentrations. However, in each sample the ratio of P:Z:T was maintained in the atomic ratio of 1:0.52:0.48.^[2]

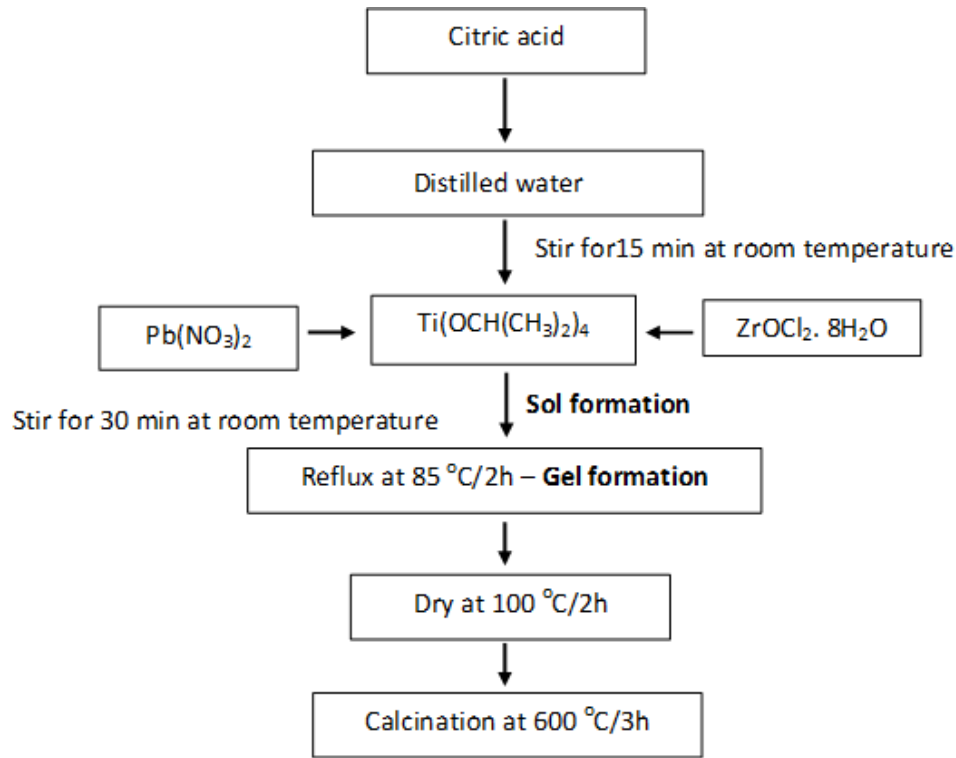


Figure 1: Flow chart of preparation of PZT powders by sol-gel route



Figure 2: Sample 1



Figure 3: Sample 2



Figure 4: Sample 3

To make the dielectric, 2 wt% of the PZT powders was dispersed in diethylene glycol and stirred with heating to obtain a homogenous solution for about 2 hours at a bath temperature of 50°C . The solution was homogenized using a homogenizer and subjected to ultrasonic vibrations.

2.2 Characterization of PZT

2.2.1 X-Ray Diffraction

X-ray diffraction of the three samples of PZT was carried out and the results were compared to the standard XRD pattern of PZT composite obtained from other methods.

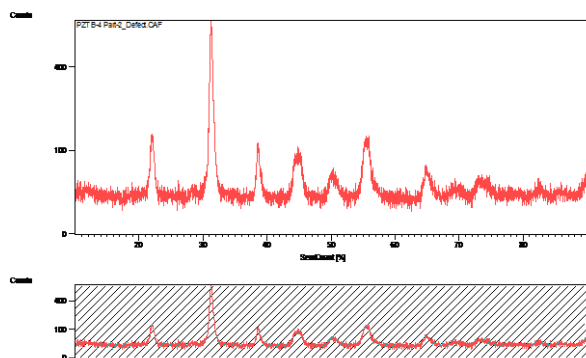


Figure 5: XRD pattern of Sample 1

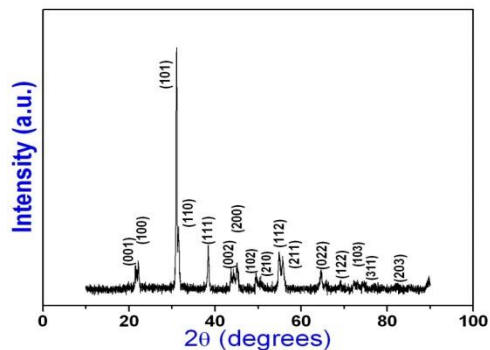


Figure 6: Standard XRD pattern of PZT

Comparison of XRD pattern of sample PZT and standard PZT

Of the three samples, sample 1 showed the closest resemblance to the standard pattern. The figures are shown above (Figure 5 & Figure 6). As you can see, the XRD patterns are very similar. Thus, it can be concluded that the low temperature synthesis of PZT was successful in producing the same powder which is otherwise obtained by more expensive methods and at higher temperatures.

2.2.2 Scanning Electron Microscopy (SEM)

The SEM images show particle sizes of around 500 nm. It was found that this PZT powder formed a colloidal solution with Diethylene Glycol (DEG) and if left for a day, some of the powder settled. To avoid this, a particle size of a smaller diameter was required.

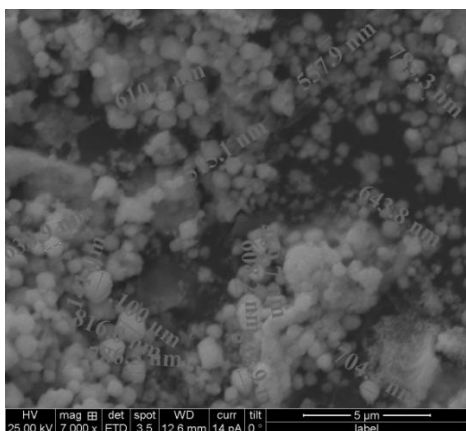


Figure 7: SEM image of PZT sample

The powder was mixed with a non-dissolving liquid, namely acetone and then crushed in a simple mortar and pestle. The particle size was reduced to 100-200nm. 2 wt% of this powder was dissolved in DEG. It was homogenized and further subjected to ultrasonic vibrations to give a clear homogeneous solution.

2.3 Fabrication of the Supercapacitor

The Liquid dielectric was placed in sample holders of different shapes and sizes which would give us a good understanding of its effects on the performance of supercapacitors.

2.3.1 Supercapacitor 1



Figure 8: Supercapacitor 1

The sample holder in figure 8 was made of plastic. It was completely filled with the dielectric. The diameter is 1.2 cm and the height is 3.6 cm. Simple copper wires were used as the anode and cathode. It was held in place and sealed using a water resistant sealant. The cap denotes the positive terminal.

2.3.2 Supercapacitor 2



Figure 9: Supercapacitor 2

The sample holder in figure 9, also made of plastic, was filled up completely with the dielectric. This holder is larger than the supercapacitor 1. The diameter of the holder was 3 cm and the height was 4.5 cm. Similar copper wires were used as the electrodes. It was tightly sealed using a sealant as done in the previous one. The cap denotes the positive terminal of the supercapacitor.

2.3.3 Supercapacitor 3



Figure 10: Supercapacitor 3

This sample holder is different from the other two. The diameter is larger at 3.9 cm, and the height is much smaller at 1.4 cm.

The case was insulated thoroughly to prevent any leakage. Similar copper wires were used as electrodes.

III. RESULTS AND DISCUSSIONS

3.1 Capacitance

The capacitance was found using an LCR meter. It was measured for all the supercapacitors which yielded the results as shown in Table 1.

Table 1: Capacitance

Form factor	capacitance
Supercapacitor 1	17 pF
Supercapacitor 2	35 pF
Supercapacitor 3	253 pF

The sharp increase in the capacitance of supercapacitor 3 can be attributed to the fact that C is directly proportional to A/d as seen from equation (1).

$$C = \epsilon(A/d) \dots\dots\dots(1)$$

Where,

C=capacitance of the capacitor

ϵ = Dielectric permittivity

d=Distance between the electrodes

The capacitance can be further increased by arranging similar such capacitors in parallel. When capacitors are kept in parallel, their effective capacitance is given by,

$$C_{\text{eff}} = C_1 + C_2 + C_3 \dots\dots\dots(2)$$

Combining supercapacitors in series or parallel has an advantage over regular batteries as it does not require cell balancing. Hence, a supercapacitor of any desired capacitance and voltage can be attained by simply arranging them in parallel.

Another way of increasing the capacitance of the supercapacitor is by varying the dimensions of the sample holder. From equation (1), we see that increasing the area of the electrodes and reducing the length between the electrodes can increase the capacitance by a big margin. Thus, the use of carbon electrode instead of copper electrodes would result in a far more superior capacitance. It is said that the surface area of 1 gram of carbon is equivalent to the area of a tennis court.

3.2 Relative permittivity

The relative permittivity of the dielectric was calculated using the following formula:

$$\epsilon_r = (C*d)/(\epsilon_0*A) \dots\dots\dots(3)$$

Where,

C= Capacitance of the capacitor

d= Distance between the electrodes

A= Surface area of electrode

$$= \pi * d * l$$

$$= \pi * (0.0008) * (1) = 0.0025 \text{ m}^2 \dots\dots\dots(4)$$

$$\epsilon_0 = \text{Electric constant} = 8.854 * 10^{-12} \text{ Fm}^{-1}$$

Thus, the relative permittivity ϵ_r was found to be 7078 which is high when compared to a capacitor.

3.3 Voltage

The maximum voltage of the supercapacitors was found using a multimeter after being charged completely. The voltage was recorded and displayed in table 2.

Table 2: Maximum Voltage

Form factor	Voltage (volts)
Supercapacitor 1	0.3
Supercapacitor 2	0.66
Supercapacitor 3	0.5

As you can see, the voltage is the largest for Supercapacitor 2 and least for supercapacitor 1. Comparing the volumes of the liquid dielectric held by each of these supercapacitors, we notice that the voltage is directly proportional to it. Thus, more the volume of dielectric, more is the voltage. Since supercapacitor 2 has the largest volume of the dielectric among the three, it shows the highest voltage rating. Hence we can conclude that the voltage can be increased by using more of the liquid dielectric.

3.4 Energy stored, W_{stored}

The maximum energy that can be stored was calculated using the formula

$$W_{\text{stored}} = C*(V)^2/2 \dots\dots\dots(5)$$

Where, C= capacitance in Farads

V= voltage in Volts

Table 3: Maximum energy storage capacity

Form factor	W_{stored} (J)
Supercapacitor 1	$7.65 * 10^{-13}$
Supercapacitor 2	$7.623 * 10^{-12}$
Supercapacitor 3	$3.1625 * 10^{-11}$

Clearly the 3rd supercapacitor has a much higher energy storage capacity due to the superior capacitance.

Charge & Discharge

The time taken for all the 3 supercapacitors to reach its full charge is about 2 minutes. This is much faster than a conventional battery which requires to be charged for hours. But

consequently, the discharge rate is much faster when compared to a battery. Also, supercapacitors self-discharge to some extent if not used.

IV. APPLICATIONS

There are numerous applications that could use the proposed technology. For instance, small size supercapacitors can be widely used as maintenance-free power sources for IC memories and microcomputers. Among applications for large size supercapacitors are load leveling in electric and hybrid vehicles as well as in the traction domain, the starting of engines, applications in the telecommunication and power quality and reliability requirements for uninterruptable power supply (UPS) installations [1]. Supercapacitors, owing to their high power capability, allow new opportunities for power electronics. Applications where short time power peaks are required can be provided by supercapacitors. Typical examples where a big current is required during a short time are the fast energy management in hybrid vehicles or the starting of heavy diesel engines. Supercapacitors may supply the power to the electrical vehicle required to meet the city road traffic conditions. Additional applications may be found in elevators, cranes or pallet trucks in the electric transportation domain, hand tools, flashlights, radars and torpedoes in the military domain, defibrillators and cardiac pacemakers in the medicinal domain, pulsed laser and welding in the industry and memory supplies in phones or computers.

V. CONCLUSIONS

Thus, from the above study it can be concluded that the supercapacitor made using a Liquid Composite as the dielectric is a viable and stable alternative to solid state supercapacitors. There are some advantages which support this fact. For example, the dielectric permittivity can be easily tuned by increasing the weight percentage of PZT in DEG or by varying the particle size. The particle size, in turn, can be changed by just varying the calcination temperature. Usage of the PZT powder is very less; 2 wt% to be precise. Thus the Dielectric can be made with relatively low costs. Also, the material is non-corrosive and is inert to any electrode material. So other electrodes like carbon or Ag can also be used. Since the dielectric is in liquid state, the final product can take any shape to suit the needs of different applications.

So as we can see, the future of LCDM supercapacitors is looking very bright and there is immense scope to carry out further research and improve this technology, which could perhaps lead to replacement of Lead acid or any other harmful form of batteries in the future. We intend on continuing our research further on this topic and hope to acquire some more useful data.

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