

## **FABRICATION OF POLYMER FREE CERAMIC ELECTROLYTE FOR DYE-SENSITIZED SOLAR CELLS**

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### **ABSTRACT**

This study was carried out in order to prepare a mineral filler, which in turn can fully or partially replace the need of polymers in polymeric gel electrolytes in Dye sensitized Solar Cells (DSSCs). Electrolytes with ceramic fillers possess many advantages over the polymeric electrolytes used in the DSSCs. Since the constituents of this filler are completely non-toxic, the adverse effects on the environment can be neglected. Moreover, they possess excellent mechanical, thermal and chemical properties, which in turn enhance the overall stability of the device. In this article, we report for the first time, the possibility of using a mixture of ceramic minerals, kaolinite, feldspar and quartz filler in preparation of polymer-free quasi-solid electrolytes for DSSCs. According to our preliminary studies, the DSSCs comprising with optimized mixture of above minerals showed an overall efficiency of 3.62% with a filling factor of 66.4%. The open circuit voltage ( $V_{oc}$ ) and the short-circuit current density ( $J_{sc}$ ) values were 624 mV and 8.77 mA cm<sup>-2</sup> respectively. The room temperature conductivity of the electrolyte was in the order of  $1111 \times 10^{-4}$  S cm<sup>-1</sup>. The charge transfer resistance in the electrolyte - photoanode interface and the electron life time in the DSSC comprising with novel electrolyte determined by Electrochemical Impedance analysis was 333 ohms and 12.54 ms which are in agreement with the typical values of the DSSCs fabricated with most of the polymeric gel electrolytes.

### **1. INTRODUCTION**

The inert nature of ceramic electrolyte is highlighted widely as a factor which enables replacement of liquid and polymer electrolytes to ceramic electrolytes in many electrochemical devices such as photovoltaic cells, electrochromic displays and batteries [1]. The manufacturing cost of these devices will reduce in return due to the low-cost associated in the production of ceramic electrolytes. Moreover, usage of electrolyte with ceramic fillers instead of polymeric or liquid electrolytes in these devices will really solve the stability, corrosion and sealing problems associated with these devices. On the other hand, the ceramic filler electrolytes (CFE) are biodegradable and therefore, it is an environmentally friendly alternative to that of polymer electrolytes of which certain bio-hazardous properties have been discovered [2-4]. Polymer electrolytes seem to contain a considerable level of toxicity even in the most widely used polymers such as Polyethylene Oxide (PEO) [3]. Rigid cell designs similar to that of thin-film-based devices can also be fabricated from CFEs owing to the high elastic moduli. CFEs operate efficiently at higher temperatures since at elevated temperatures the ionic conductivity increases as a result of the supply of energy to the ionic point defects. However, some ceramic electrolytes work equally effectively even at comparatively low temperatures with the addition of ceramic particles in controlled amounts [5]. The significant thermal stability and high ionic conductivity levels of CFEs enable them to be used in a wide variety of batteries for Electric Vehicles (EVs) and Hybrid Electric Vehicles (HEVs) [6]. The features found in CFEs such as compactness, low weight and

less inflammability are core values which the automobile manufacturers are tirelessly pursuing to develop batteries. Basically, due to the less frequent maintenance and the low space consumption of the ceramic electrolyte, the electrochemical cells can be easily mounted without excessive visibility to the outside. The low-inflammability of the ceramic electrolyte ensures its safe and secureness even at the most extreme conditions. The dendrite growth which is one of the key factor affecting the conductivity in polymer electrolytes does not occur in ceramic electrolytes [6]. The operability of ceramic electrolytes at elevated temperatures are found attractive by specific industries since their processes are carried out at the said conditions [7].

Therefore, by considering all the above facts we have explored the possibility of use of CFEs in Dye Sensitized Solar Cells (DSSCs) and according to our knowledge for the first time here we report our preliminary studies as possible usage of CFE in DSSCs as an alternative to polymeric electrolyte the those devices.

## **2. EXPERIMENTAL**

Different compositions of ceramic fillers were prepared by using Kaolinite, Feldspar and Quartz. An optimized mixture was obtain through the mixture of Kaolinite, Feldspar and Quartz in 41%, 36% and 23% by weight composition respectively. The obtained mixture was thoroughly mixed using a mortar and pestle adding controlled amounts systematically. The particle size was reduced using an electrical mortar and pestle for about thirty minutes until the particle size reduces to less than 10  $\mu\text{m}$ . After obtaining the mixture, the sedimentation process was carried out in accordance with the 'Stokes' law for a precise forty eight hours to filter out particles less than 1.2 $\mu\text{m}$  in size. Before carrying out this process a deflocculant, Sodium Hexametaphosphate (SHMP) was added to the solution to prevent the minute particles from getting flocked together which might lead to erroneous sedimentation eventually resulting to an artificial alteration in results [8]. Observations were done using five sample solutions in order to determine the precise amount of deflocculant needed. The ratio between the identically concentrated initial solution and the deflocculant was found to be 10:1. The range of 0.2% - 0.5% deflocculant agent by weight of the initial sample, was determined through a literature review [9]. Accordingly, the sample solutions with different deflocculant agent amounts were prepared. Then the obtained solution, without the precipitate was dehydrated with the use of a rotary evaporator till only a small amount of moisture was available in the sample since excessive moisture removal leads to plastering of the mixture on to the wall of the rotary evaporator bulb. The highly concentrated solution was then placed in an oven, in a petri dish to facilitate effective evaporation by heat and increased surface exposure. At the point of which the solution was transformed into a semi solid state, the solution was removed from the oven and was placed inside a desiccator for eighteen hours to slowly remove the moisture out of the sample. This was done because fast removal of moisture results in clustering of particles. After totally removing moisture out of the sample, the completely dried out powder was collected into a test tube and was sealed off. This was done since the small particles tend to absorb moisture from the environment easily. The obtained powder was then mixed with an optimized mixture of Ethylene Carbonate (EC), Propylene Carbonate (PC), Tetrapropylammonium Iodide, Potassium Iodide (KI), and Iodine ( $\text{I}_2$ ), with amounts of 0.1000g, 0.4000g, 0.4000g, 0.023g, 0.0487g and 0.0057g respectively, for a single run. Finally, the complete mixture was stirred overnight using a magnetic stirrer [10].

Impedance analysis were carried out on the above CFE using Metrohm Autolab PGSTAT18N instrument at various temperatures in the range between 25  $^{\circ}\text{C}$  and 60  $^{\circ}\text{C}$  using a vacuum oven.

In order to apply this CFE in DSSCs, dye absorbed photoanodes were prepared as follows. Kind of compact layer of TiO<sub>2</sub> was obtained on pre-cleaned fluorine-doped tin oxide (FTO) glass substrate by spin coating of a solution containing 0.25g of TiO<sub>2</sub> (Evonic P90 Aeroxide) with 0.1 mol dm<sup>-3</sup> of HNO<sub>3</sub>. Then the substrate with TiO<sub>2</sub> layer was sintered at 450 °C for 45 minutes. Consequently, another layer of TiO<sub>2</sub> was fabricated on top of the compact layer by using a paste prepared with 0.25g of TiO<sub>2</sub>, 0.02g of Triton X-100, 0.05g of PEO 1000 (Fluka) and 0.1 mol dm<sup>-3</sup> of HNO<sub>3</sub> by “doctor blade” method and subsequently re-sintered at 450 °C for 45 minutes and allowed to cool down to the room temperature before immersing in the ethanolic ‘N719’ dye for 24 hours. For the ease of calculations as well as due to the fracturing of the edges with time, a specific area was (0.25 cm<sup>2</sup>) selected out of the fabricated layers. The electrolyte was then sandwiched between the FTO/TiO<sub>2</sub> and Pt/FTO configuration. Current-voltage (I-V) measurements were obtained using a solar simulator with an illumination of a 100 mW cm<sup>-2</sup> Xenon 500 lamp, along with an attached AM 1.5 filter [11]. The Electrochemical Impedance Spectroscopy (EIS) analysis was performed using the Metrohm Autolab PGSTAT128N by which the measurements were interpreted as an equivalent circuit.

### 3. RESULTS AND DISCUSSION

Fig.1 shows the variation of the conductivity of the CFE at different elevated temperatures in the typical ln(σT) vs 1000/T plot.

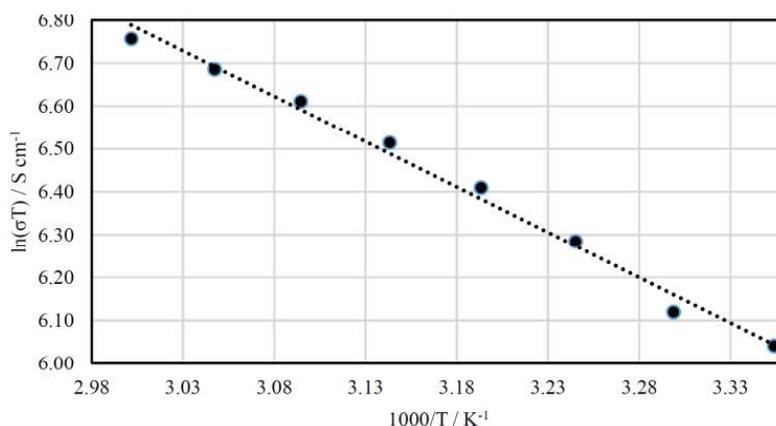


Fig.1. Conductivity variation of CFE in the form of ln(σT) vs 1000/T.

In accordance to the Arrhenius equation, the resistance has decreased uniformly with the increment of temperature. Since resistivity is proportional to the resistance, it has followed in a similar trend opposing to that of conductivity. Impedance analysis showed  $1.41 \times 10^{-2} \text{ s cm}^{-1}$  conductivity at the room temperature (25°C).

Fig.2 shows the Current-Voltage characteristic of the DSSC comprising with CFE. The DSSC showed an overall efficiency of 3.62% with a filling factor of 66.4%. The open circuit voltage (Voc) and the short-circuit current density (Jsc) values were 624 mV and 8.77 mA cm<sup>-2</sup> respectively. Even though we have not checked the stability of the device for prolonged time preliminary studies showed a remarkable stability as in the devices with polymeric electrolytes.

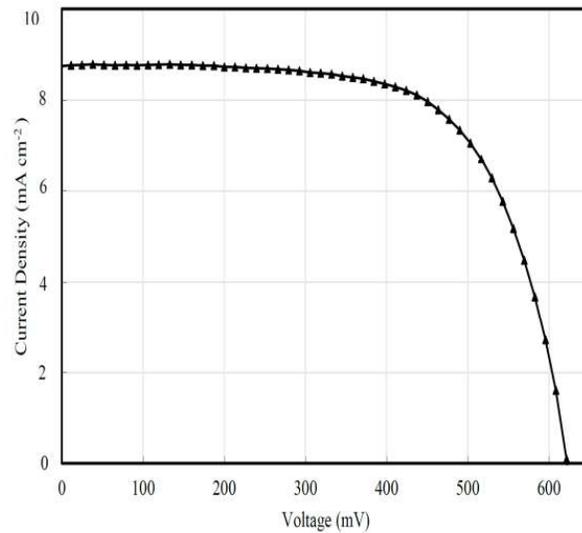


Fig.2. Current- voltage characteristics of the DSSC prepared with ceramic filler electrolyte.

In order to evaluate the interfacial charge transfer resistances of the device with new electrolyte, DSSCs were investigated by EIS measurements. The Nyquist plot of the DSSC with above electrolyte is shown in Fig.3 with the corresponding equivalent circuit used to estimate the charge transfer values. The estimated values of the

the series resistance ( $R_S$ ), charge transfer resistance of the Pt/electrolyte interface ( $R_{1CT}$ ) and charge transfer resistance of the  $TiO_2$ /electrolyte interface ( $R_{2CT}$ ) for the device are tabulated in table 1. These results show that the series resistance as well as the charge transfer resistance values at the two electrode/electrolyte interfaces of the DSSC fabricated with this electrolyte are in the same order as in the case of PAN based polymer electrolytes [13].

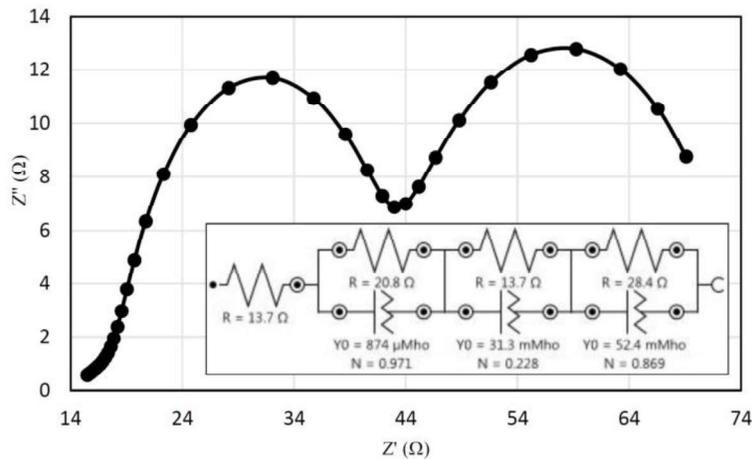


Fig.3. Nyquist plot of the DSSC with ceramic filler electrolyte and the equivalent circuit used to estimate the resistance values.

Table 1. Series resistance ( $R_s$ ), charge transfer resistance of the Pt/electrolyte ( $R_{1CT}$ ), charge transfer resistance of the  $TiO_2$ /electrolyte ( $R_{2CT}$ ) of DSSCs with ceramic filler and PAN based electrolytes.

	DSSC with Ceramic Filler Electrolyte	DSSC with PAN based gel electrolyte [ 13 ]
$R_s$ ( $\Omega$ )	13.7	15.22
$R_{1CT}$ ( $\Omega$ )	20.8	30.51
$R_{2CT}$ ( $\Omega$ )	13.7	46.18

The electron life time is estimated from the Bode plot as shown in Fig.4.

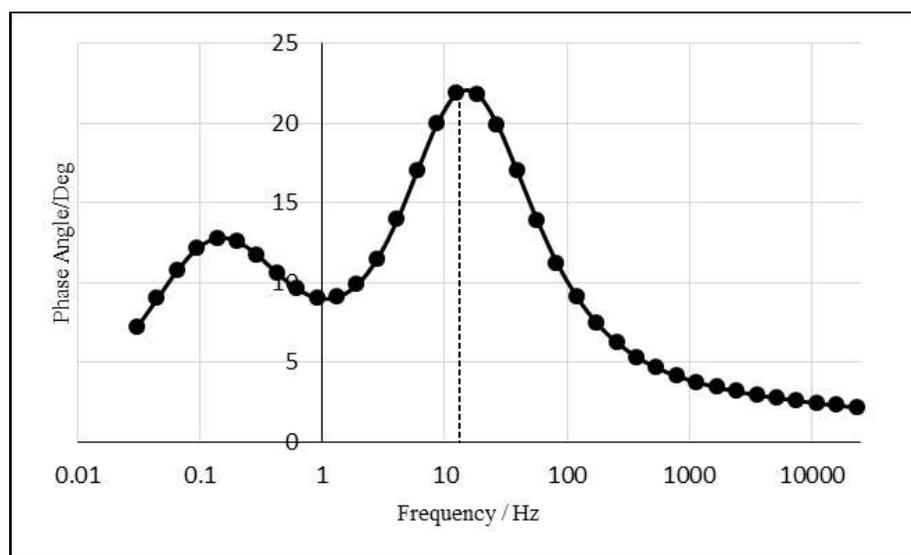


Fig.4. Bode plot extracted from EIS measurements of the DSSC with ceramic filler electrolyte.

From the Bode plot the highest peak of the plot was observed to be at frequency 12.649 Hz, thus the electron life time is 12.582 ms which is also in the same order of the electron life time of the DSSC with polymer electrolytes [ 14].

#### 4. CONCLUSION

The usage of the deflocculant agent (Sodium Hexametaphosphate - SHMP) is the most important step in obtaining the optimized ceramic electrolyte with particle size less than 1.2  $\mu\text{m}$ . The electrical and electronic features of the mixture looks promising and shows a great potential to improve upon with further changes to the structure as well as the composition of the mixture. Ceramic electrolyte usage in solar cells is a cost-efficient, eco-friendly and a sustainable approach to ever increasing energy demand.

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