Potential of Tebalan Shells from Tuban Beach as Active Material in Perovskite Solar Cells

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Abstract *- One source of environmentally friendly renewable energy that has begun to be widely developed is PSC (Perovskite Solar Cell) made from natural ingredients. PSC is a new breakthrough strategic mineral processing technology as an alternative to silicon in the industry of solar power safety and stability. PSCs are easier to manufacture compared to silicon-based solar cells. The PSC material in this research is perovskite* $CaTiO_3$ *which is made from the reaction between calcium carbonate (*$CaCO_3$*) which is obtained from the Tebalan shell powder of Tuban beach and titanium dioxide (*TiO_2*). The method used in this research is substrate preparation, synthesis of Perovskite* $CaTiO_3$*, making* TiO_2 *paste*$_2$*, electrolyte solution preparation, counter electrode preparation, fabrication perovskite solar cell (PSC), as well as testing, characterization and data analysis. The tests and characterization that will be carried out are: Crystal structure of powdered materials used in making perovskite solar cells using XRD (X-ray Diffractometer) type X-Pert*^{3} *Powder, testing electric current with a potentiometer, and measuring light with a lux meter. The results of XRD testing on the calcined powder showed that the structure of calcium titanate perovskite (*$CaTiO_3$*) was as much as 68.2%. Meanwhile, the characteristic values of the electrical properties of Tebalan clam shell perovskite solar cells from the lamp light source data obtained show that* V_m *and* I_m *Daylight lamps have a greater value than warm white lamps and the efficiency value of the solar light source is highest when shown Air Mass 1.5, which is 0.000127%.*

Keywords*: Calcium Carbonate (*$CaCO_3$*); Calcium Titanate (*$CaTiO_3$*); Perovskite Solar Cell (PSC); Tebalan Shell*

INTRODUCTION

Currently, energy needs are increasing greatly along with population growth. Utilization of fossil fuel energy sources has been widely used. However, the increasing need for energy causes fossil fuels to run out. There is a need for alternative energy to meet the increasing energy needs. One of the renewable energies currently being developed is the use of solar energy. Solar sources have photovoltaic cells that can convert solar energy into electrical energy. Solar cells are devices that can convert solar energy into electrical energy (Et-taya et al., 2020).

The solar cells that researchers had previously developed were dye sensitized solar cells (DSSC) which were later developed into *perovskite solar cells* (PSC). PSC solar cells are made from a mixture of halide-organic/inorganic materials which have a perovskite structure. The efficiency of PSC reached up to 23% in recent years (Chen et al., 2019). The structure of perovskite-based solar cells (PSC) consists of perovskite material which acts as a light absorber, conductive glass as a substrate (anode) which usually uses *Indium Tin Oxide* (ITO) or *Fluorine Tin Oxide* (FTO), semiconductor material as an electron donor *electron transport material* (ETM), electrolyte as an electron acceptor *hole transport material* (HTM) and carbon as a reference electrode (Mesquita et al., 2018). The crystal structure of generally widely used PSC compounds such as $CH_3NH_3PbI_3$, $CH_3NH_3PbCl_3$, $CH_3NH_3PbBr_3$, $CH_3NH_3PbGeCl_3$, and $CH_3NH_3PbSnCl_3$

(Herna et al., 2022). The presence of lead (Pb) in the perovskite type compounds used is very toxic and dangerous. This makes researchers continue to innovate to produce solar cells with safe and environmentally friendly materials to produce high efficiency.

The material calcium titanate ($CaTiO_3$) with a perovskite structure applied to suya cells has been developed by researchers in recent years. $CaTiO_3$ can be obtained from the reaction between calcium carbonate ($CaCO_3$) and titanium dioxide (TiO_2) via method *come left*. Calcium carbonate is found in natural limestone and the shells of living creatures. One shell that has a high calcium carbonate content is clam shells. Research by Mijan et al. mentions that clam ale-ale shells Contains up to 95% calcium composition so it has the potential to be used as a raw material for the manufacture of calcium titanate (Hariyati and Wibowo, 2019). Calcium content in the shell with a size of 200 mesh and calcined temperature 900°C for 4 hours has a percentage of more than 60% (Hossain et al., 2011; Torimtubun et al., 2018). Calcium carbonate in clam shells can be purified in form *Precipitated Calcium Carbonate* (PCC). Much research has been carried out in making PCC materials. The best PCC material can be synthesized using this method *solid-liquid* carbonation using carbon dioxide gas (Zein and Riza, 2022). Making PSC material using oyster shell powder as raw material through a process of cleaning, drying, grinding 200 mesh and calcining at a temperature of 900°C for 4 hours (Kemal, 2020; Puspita, 2018). $CaTiO_3$ perovskite solar cells was successfully produced with the highest efficiency of up to 2.04% (6). The research results show that the process of making $CaTiO_3$ has a big influence, namely the heating process at a certain temperature causes the $CaTiO_3$ crystal structure changes shape from orthorhombic to tetragonal and to cubic at higher temperatures.

The current perovskite development is still minimally based on nature. Many commercial perovskites developed are still silicon-based and contain dangerous and toxic compounds such as lead (Pb) (Ramli et al., 2022). There is a need for environmentally friendly compounds in the development of perovskite solar cells such as perovskite $CaTiO_3$ nature-based. Perovskite $CaTiO_3$ can be obtained from clam shells. The latest in this research is the use of calcium carbonate ($CaCO_3$) from thick shells from Tuban Beach. Calcium carbonate will be reacted with titanium dioxide (TiO_2) via method *come left* to form $CaTiO_3$ perovskite Which then applied to *Perovskite Solar Cell* (PSC).

RESEARCH METHODS

The methods of this research include substrate preparation, synthesis of perovskite $CaTiO_3$, making TiO_2 paste, making electrolyte solutions, counter electrode preparation, fabrication *perovskite solar cell* (PSC), and the last is testing and characterization and data analysis.

1. Substrate Preparation

The substrate used is TCO (*Transparent Conductive Oxide*) glass of the ITO (*Indium Tin Oxide*) type. The ITO measured 1×2 cm^2 on the conductive part so that an area of 1×2 cm^2 is formed. The dimensions of the substrate used can be seen in Figure 1.

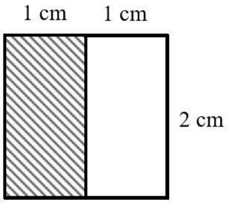

Figure 1. Substrate ITO (*Indium Tin Oxide*)

2. Synthesis of Perovskite $CaTiO_3$

The material calcium titanate ($CaTiO_3$) with a perovskite structure begins by preparing calcium carbonate ($CaCO_3$) which is obtained from Tebalan clam shell powder. The shells are washed with running water and then dried under the sun. After that, the shells are crushed to produce a finer size and sieved using a 200mesh sieve to separate small and uniform particles. Next, the shellfish powder was calcined at 500°C for 4 hours to produce the $CaCO_3$ compound. Calcination results were characterized using XRD. Calcium Titanate ($CaTiO_3$) can be synthesized from the calcination process of calcium carbonate ($CaCO_3$) from tebalan shells and titanium dioxide (TiO_2) with a composition of 48.3% $CaCO_3$ and 51.7% TiO_2 (Puspita, 2018). $CaCO_3$ powder and TiO_2 powder dissolved in ethanol and stirred thoroughly *magnetic stirrer* for 2 hours at room temperature. The slurry was dried in an oven at 100ºC for 1 hour. The mixed powder was ground then calcined with a furnace at 900°C for 2 hours with a ramp rate of 10°C/minute to obtain $CaTiO_3$ fine powder (Handayani and Syahputra, 2017). The process of making $CaTiO_3$ paste This is done by mixing 1 gram of $CaTiO_3$ powder with 2.5 ml ethanol. The two ingredients are stirred using *magnetic stirrer* until the solution becomes homogeneous.

3. Making TiO_2 paste

TiO_2 paste preparation stage carried out using a thick layer technique by mixing 3.07 grams of polyvinyl alcohol (PVA) into 30 ml of distilled water, then stirring it for 30 minutes at a temperature of 40◦C using *magnetic stirrer*. Then, 3.10 grams of TiO_2 powder added until a paste forms. The viscosity of the paste is regulated by the amount of binder used.

4. Making Electrolytes

The electrolyte is made by mixing 0.8 grams of Potassium Iodide (KI) 0.5M with 9 ml of acetonitrile and 1 ml of distilled water. Then Iodine (I_2) 0.05 M as much as 0.127 grams into the solution, then stir using *magnetic stirrer* for 30 minutes and stored in a closed bottle or in a bottle that has been covered with aluminium foil (Maulana and Prakasa, 2021). The application of the electrolyte solution to TCO glass which has been coated with TiO_2 and $CaTiO_3$ is carried out using a dropper with five drops.

5. Manufacturing Opposite Electrode

This process is carried out by burning the conductive part of the TCO glass using a candle flame until the TCO glass is evenly coated with carbon. Burning is carried out for approximately 1 minute (Maulana and Prakasa, 2021).

6. PSC Fabrication

PSC fabrication begins by depositing TiO_2 paste on ITO measuring 1×2 cm^2 on the conductive part so that an area of 1×1 cm^2 is formed as in Figure 3. The deposition process is carried out using the method *spin coating*. The layer formed was dried for 15 minutes and burned in an electric oven at a temperature of 150◦C for 30 minutes. Then the conductive glass is coated with TiO_2 paste recoated with $CaTiO_3$ perovskite. Furthermore, combination of TCO glass coated with TiO_2 paste give $CaTiO_3$ (as an anode) with TCO glass coated with carbon from burning candles (as a cathode). The final stage is adding the iodine solution to the glass surface coated with TiO_2 paste give perovskite $CaTiO_3$, then the two conductive glasses are joined together with a paperclip, just like the arrangement sandwiches (Figure 2). The solar cells that have been assembled are then dried under a light source.

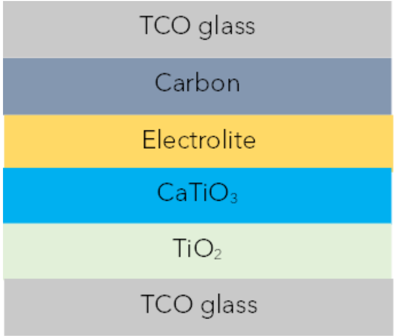

Figure 2. Arrangement Perovskite solar cell

7. Material Characterization

Material characterization using XRD (*X-ray Diffractometer*) type X-Pert[3] Powder for know the characteristics of the crystal structure of the powdered materials used in manufacture *perovskite solar cell*, testing electric current with a potentiometer and measuring direct light and 15Watt halogen lamps through *luxmeter*.

8. Data analysis

Data analysis was carried out based on data from XRD and electric current testing results. Data analysis in this research is presented in the form of pictures, tables and graphs to make it easier to carry out data analysis and adapted to the literature review that has been reviewed to be able to conclude the results of this research and provide suggestions for research. To analyse XRD test results to determine the structure of materials using software *Match!*.

RESULTS AND DISCUSSION

Perovskite Material Structure Tebalan Clamshell

Thick clam shells are used as active material in perovskite solar cells, synthesized by making $CaCO_3$ powder from the calcination process at 500°C for 4 hours which is known from the XRD test results in Figure 3.

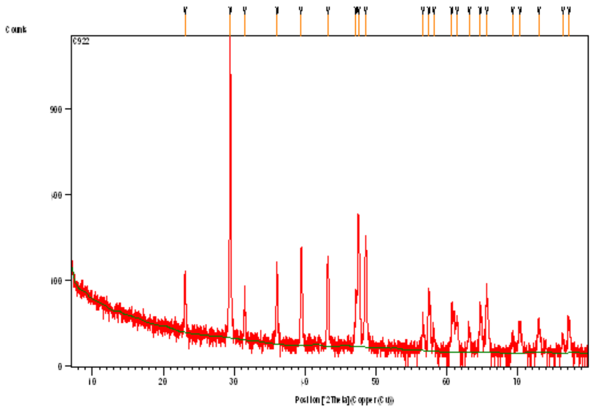

Figure 3. Graph of XRD results on Tebalan clam shell powder

The XRD results of thick shell powder in Figure 3 show that the crystal structure of $CaCO_3$ The result is a calcite structure with the highest peak at 2θ 29.4095°. These results are based on data processing in the software *match!* with database reference COD-Inorg REV189751 2017.01.03. The resulting calcite structure has a trigonal crystal system with a mass density of 2.705 g/cm³. Perovskite material is produced from $CaCO_3$ powder which has been synthesized from thick clam shells mixed with TiO_2 powder. The perovskite results are shown from XRD testing in Figure 4.

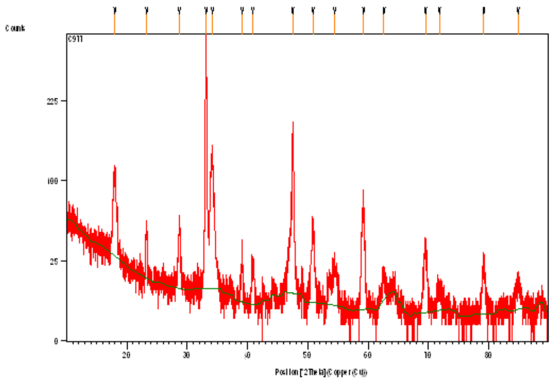

Figure 4. XRD graphs of powder $CaTiO_3$

Based on software processing *match!* XRD results of $CaTiO_3$ powder has 2 phases with a calcium titanate perovskite structure ($CaTiO_3$) 68.2% and portlandite ($Ca(OH)_2$) 31.8% based on COD-Inorg database reference REV189751 2017.01.03. The percentage of perovskite produced is in accordance with Torimbutun's research, namely 60% (Torimtubun et al., 2018). The resulting perovskite structure is used as an active material in solar cells. $CaCO_3$ mixing and TiO_3 through a calcination process of 900°C for 2 hours can produce more than 50% perovskite calcium titanate ($CaTiO_3$). The perovskite crystal system produced in this research is orthorhombic with a mass density of 4.03 g/cm³.

Electrical Properties of Tebalan Clamshell Perovskite Solar Cells

Characteristic values of the electrical properties of thick clamshell perovskite solar cells are shown in figure 5 and Table 1. Thick clamshell PSCs were fabricated with TiO_2 thickness of 45 mm. Lamp light is used to determine the effect of differences in light spectrum characteristics, changes in light intensity levels on PSC output. The types of light spectrum used are Cool Daylight LED and Warm White LED. Maximum power is the greatest result of multiplying the current (I) by the voltage (V) of the PSC when load variations vary to form an I-V curve. The current and voltage obtained are symbolized by I_m and V_m. Table 1 is the result of calculating I_m and V_m PSC with a lamp light source.

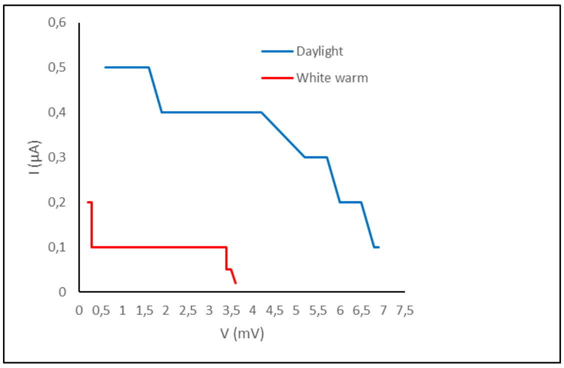

Figure 5. Test results for voltage and current values with a lamp light source

From the light source data obtained, it shows that I_m and V_m in daylight lamps have greater values than in warm white lamps. This shows that the greater the light intensity given, the values of I_m and V_m increase. This result is influenced by the presence of light provided by daylight lamps which have 1080 lumens with a light wavelength of 365-450 nm (Lazzarin, 2023).

Table 1. Calculation results of Im and Vm PSC with a lamp light source

Light Source	PSC TiO2 45 mm	
	V_m (mV)	I_m (µA)
Daylight	5,7	0,3
White warm	3,4	0,1

I_m and V_m measurements which can affect the FF value and PSC efficiency are also carried out using direct sunlight (figure 6). After carrying out several measurements, I_m and V_m PSC were obtained from solar light sources with different intensities. Treatment was carried out in the morning, afternoon and evening.

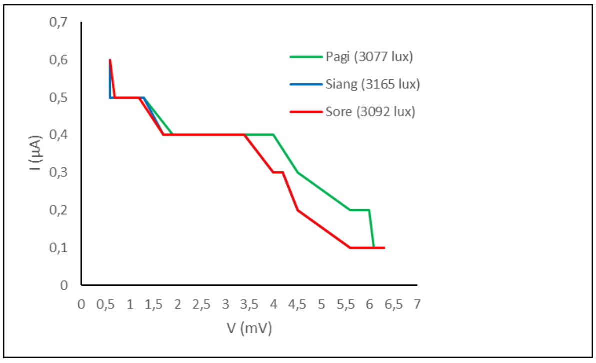

Figure 6. Test results for voltage and current values with a sunlight source

Table 2. Calculation results of I_m and V_m PSC with a solar light source

Intensity (lux)	PSC TiO2 45 mm	
	V_m (mV)	I_m (µA)
79700	4	0,4
82050	3,4	0,4
80400	3,4	0,4

Table 2 shows the results of I_m and V_m from solar light sources using load variations. Measurements were taken in the morning *Air Mass* AM 1.5 at 08.00-09.00 with a sunlight intensity of 79700 lux, noon 12.00-13.00 with a sunlight intensity of

82050 lux and in the afternoon 15.00-16.00 with a sunlight intensity of 80400 lux. The results obtained show that the V_m and I_m values are the highest at time *Air Mass* 1,5.

The results of measuring the efficiency of thick clam shell PSCs using Cool Daylight LED and Warm White LED light sources are shown in Table 3.

Table 3. PSC efficiency with lamp light sources

Characteristic	PSC TiO2 45mm	
	daylight	white warm
I_m (A)	0,0000003	0,0000001
V_m (V)	0,0057	0,0034
I_{sc} (A)	0,0000007	0,0000002
V_{oc} (V)	0,012	0,007
Fill factor (%)	20,36	24,29
Effficiency (%)	0,0001007	0,0000402

The results of measuring the efficiency of PSC Tebalan clamshells using a sunlight illumination source are shown in Table 4. The intensity of light illumination (lux) received during the measurement varies.

Table 4. PSC efficiency with solar light sources

PSC TiO2 45mm			
Intensity (lux)	79700	82050	80400
I_m (A)	0,0000004	0,0000004	0,0000004
V_m (V)	0,004	0,0034	0,0034
I_{sc} (A)	0,0000006	0,0000009	0,0000006
V_{oc} (V)	0,012	0,0112	0,0116
Fill factor (%)	22,22	13,49	19,54
Effficiency (%)	0,000127	0,000105	0,000107

Table 4 shows that from morning to noon there is an increase in the value of sunlight intensity. Then from noon to evening there is a decrease in the value of sunlight intensity. The measurement results of the intensity of sunlight (I_r) with a LUX meter (LUX) are then converted into W/m^2 units by multiplying the I_r reading by 0.0079 (1 LUX = 0.0079 W/m^2). The amount of input power on PSC efficiency is influenced by the intensity of sunlight (Hossain et al., 2011).

The efficiency of a solar cell is determined by the FF value which can be known from measuring the maximum power (I_m x V_m) of a thick clamshell PSC. If the values of I_m and V_m increase, the efficiency value also increases. This can be seen in the results of the efficiency value of the thicker clam shell PSC as the I_m and V_m values increase for lamp light sources and sunlight sources.

The PSC efficiency value of thick clam shells with the largest source of sunlight is shown in the morning *Air Mass* AM 1.5. During the day and evening the efficiency is lower than in the morning, this can be caused by the quality of the PSC which has the weakness of being easily oxidized and its quality decreasing when exposed to light. This is comparable to research conducted by Zein Muhamad, et al, that the measurement of the efficiency value of solar cells carried out had the highest value in the morning (08.00-10.00) and then as the day progressed the efficiency value decreased and increased again in the afternoon (15.00-16.00) (Zein & Riza, 2022).

CONCLUSION

The calcium titanate perovskite used as PSC material has a phase content with a perovskite structure of 68.2%. The efficiency of a solar cell is determined by the FF value which can be known from measuring the maximum power (I_m x V_m) of a thick clamshell PSC. The PSC efficiency value of thick clam shells with a daylight lamp source is 0.0001007%, while for a warm white lamp source it is 0.0000402%. From the light source data obtained, it shows that I_m and V_m in daylight lamps have greater values than in warm white lamps. The highest efficiency value of the solar light source is shown at the time *Air Mass* 1.5, which is 0.000127%. The efficiency value of thick clamshell PSCs increases as the I_m and V_m values increase for lamp light sources and sunlight sources. The greater the intensity of light given, the values of I_m and V_m increase.

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