Fabrication of DSSC photoanode based on TiO$_2$ produced by caustic fusion of local ilmenite

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Abstract. Photoanode is an essential part in dye sensitized solar cells (DSSC). Semiconductor materials, such as TiO$_2$, ZnO, and SnO$_2$, are commonly used as photoanode material. In this study, DSSC photoanode was fabricated using TiO$_2$ obtained from Bangka ilmenite concentrate by caustic fusion method followed by water leaching, acid leaching, and sol-gel reactions. The synthesized TiO$_2$ powder has an anatase phase with a crystal size of 9.55 nm, band gap energy of 3.0 eV, spherical morphology with an average particle size of 0.53 μm, and a specific area of 138.39 m$^2$/g. The synthesized TiO$_2$ powder was found to have Fe impurities. The DSSC with TiO$_2$ photoanode synthesized in this work produced current-voltage characteristics with photoconversion efficiency of 0.75%.

Keywords: DSSC, ilmenite, TiO$_2$, caustic fusion

1. Introduction
Dye sensitized solar cell (DSSC) is a semiconductor solar cell that can convert solar energy into electric current with the principle of photoelectrochemistry. DSSC was first developed by Professor Michael Grätzel and Dr. Brian O’Regan in 1991. DSSC is different from other generations of solar cells, where light is absorbed by dye molecules attached to the semiconductor layer [1]. DSSC has a layered structure (sandwich) consisting of transparent conductive glass coated by a thin layer of semiconductor (photoanode), dye solution, electrolyte solution, sealing material, and counter electrode [2].

One of the most commonly used semiconductors in DSSC that has a wide band gap energy value is titanium dioxide (TiO$_2$). TiO$_2$ is frequently used because it is relatively inexpensive, easy to synthesize, abundant, harmless, and stable in acidic or basic environments [3]. TiO$_2$ mostly has three phases of crystal structure in nature, namely anatase, rutile, and brookite. Among the three phases, rutile is the most stable phase, while anatase is a metastable phase and tends to transform to rutile at a temperature range of 600-1000 °C depending on the size of the crystal and the level of purity. The band gap energy value for anatase is 3.2 eV, while for rutile is 3.0 eV. Rutile has a slightly lower band gap energy compared to anatase and can absorb several percent of the light in the area near infrared, but electron excitation causes holes to occur, causing long-term instability of solar cells [4,5]. One of the raw materials in nature that could be processed to obtain TiO$_2$ is ilmenite. This type of material is abundant in Indonesia, yet, ilmenite has not been utilized maximally to date. Mulyono and Soepriyanto investigated the TiO$_2$ synthesized from Bangka ilmenite, using caustic fusion process and applied in
photocatalytic activity [6]. In this study, we aim to obtain TiO$_2$ powder from Bangka ilmenite concentrate by utilizing caustic fusion method combined with a water leaching, acid leaching, and sol-gel process. The synthesized TiO$_2$ powder from these methods was then be applied as photoanode in DSSC. The physical and optical properties of the synthesized TiO$_2$ were characterized and they were correlated to the electrical properties of constructed solar cell.

2. Experimental procedure

The ilmenite concentrate used for the synthesis of TiO$_2$ came from Bangka islands with a size of -200 mesh. The caustic fusion process was conducted by mixing ilmenite with NaOH in a mole ratio of 1:4 at a temperature of 450 °C for 120 minutes. Caustic fusion products were in the form of greenish sodium salts, and then leaching process was carried out with water to remove excess NaOH. The process was continued by acid leaching using 8M H$_2$SO$_4$ at 90 °C for 90 minutes. The product produced from acid leaching was TiOSO$_4$ solution, which is a precursor for the synthesized TiO$_2$. The TiO$_2$ powder was subsequently synthesized using sol-gel method. TiOSO$_4$ precursor solution was hydrolyzed by adding distilled water with TiOSO$_4$:aquades ratio of 1:6. Next, the pH of the solution was increased by adding a 10% NH$_4$OH weak base until the pH reached 1.0 at 90 °C for 2 hours until a white precipitate of TiO(OH)$_2$ gel was formed. After settling for 24 hours the washing was conducted to neutralize the pH, then dried and calcined at a temperature of 400 °C for 1 hour to produce crystalline TiO$_2$ powder. TiO$_2$ powder was characterized using x-ray diffraction (XRD), scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDS), gas sorption and UV-Vis diffused reflectance spectroscopy (UV-Vis DRS). The TiO$_2$ synthesis was carried out at the Laboratory of Solid Oxide System, Department of Metallurgical Engineering, ITB.

TiO$_2$ paste for DSSC photoanode was made by mixing 0.26 grams of TiO$_2$ powder with 0.1 mL terpineol and triton as much as 0.2 mL as a binder solution, then stirred until thoroughly mixed. Fluorine-doped tin oxide (FTO) substrate was washed with DI water mixed with Tipol solution, deionized (DI) water, and isopropyl alcohol (IPA). DSSC photoanode was coated with a blocking layer using a screen printer, after that it was dried at 120 °C for 10 minutes, and then sintered at 500 °C for 30 minutes. TiO$_2$ paste was coated on top of the blocking layer using a screen printer and then dried at 120 °C for 10 minutes and sintered at 500 °C for 30 minutes. After the substrate was coated with TiO$_2$ paste, TiCl$_4$ treatment was then conducted by soaking the substrate in TiCl$_4$ solution at 70 °C for 30 minutes. Once completed, the substrate was rinsed with DI water and sintered at 500 °C for 30 minutes. The next process was immersion of the substrate with Z907 dye solution for 24 hours. After the immersion process was completed, the substrate was rinsed using ethanol. The thickness of the photoanode layer was approximately 22 ± 0.89 μm. DSSC counter electrodes were made by depositing platinum paste (Pt) using a screen printer and then dried at 120 °C for 30 minutes and sintered at 450 °C for 30 minutes. The finished photoanode and counter electrode were then assembled, followed by electrolyte EL-HPE injection. The next step was to seal the holes on the counter electrode using sealants and aluminum foil to prevent electrolyte leakage. DSSC performance was evaluated by measuring the current density-voltage (J-V) characteristics under sun simulator with an intensity of 50 mW/cm$^2$ equipped with AM 1.5G filter and incident photon-to-current conversion efficiency (IPCE). The fabrication process and DSSC characterizations were carried out at the Research Center for Electronics and Telecommunications, Indonesian Institute of Science.

3. Results and discussion

The chemical compositions of Bangka ilmenite, i.e. a concentrate that was used as the original material for the TiO$_2$ synthesis, was analyzed using x-ray fluorescence (XRF) characterization and the results are shown in Table 1. The composition of Bangka ilmenite was dominated by TiO$_2$ (50.80%) and Fe$_2$O$_3$ (25.80%) and a small number of impurities such as MgO, Al$_2$O$_3$, SiO$_2$, SO$_3$, MnO, and others. The XRD diffraction pattern of the synthesized TiO$_2$ powder in Figure 1 shows that the synthesized TiO$_2$ powder had an anatase phase with an average crystal size of 9.55 nm. Anatase phase was indeed expected in this study because of more photoactive than rutile [7]. In synthesizing TiO$_2$ from ilmenite concentrate,
impurities especially Fe are highly avoided so that the synthesized product has a high purity of TiO$_2$. The diffraction pattern of the synthesized TiO$_2$ powder herein did not visibly show any peaks that correspond to the presence of Fe$_2$O$_3$. The peaks of Fe$_2$O$_3$ were at 2θ, 24.32°; 33.30°; 35.78°; 41.04°; 49.62°; 54.24°; 62.60°, and 64.16° [8]. This is possibly because the Fe$_2$O$_3$ content was too small as shown in Table 2 through energy dispersive x-ray spectroscopy (EDS) testing. Fe impurity would cause a decrease in the value of $J_{sc}$ DSSC. That is because Fe impurities would make agglomerated granules and reduce the crystallinity of TiO$_2$ powder, whereas $J_{sc}$ was not only influenced by the amount of dye absorbed by TiO$_2$ powder, but it was also influenced by the grain size and crystallinity of TiO$_2$ [9].

Table 1. Chemical composition of Bangka Ilmenite

| Compound | Amount (%) |
|----------|------------|
| TiO$_2$  | 50.80      |
| Fe$_2$O$_3$ | 25.80   |
| V$_2$O$_5$ | 4.88     |
| MnO      | 2.90       |
| Al$_2$O$_3$ | 0.95    |
| SiO$_2$  | 0.73       |
| SO$_3$   | 0.63       |
| Y$_2$O$_3$ | 0.53     |
| P$_2$O$_5$ | 0.40    |
| Nb$_2$O$_5$ | 0.39    |
| ZrO$_2$  | 0.16       |
| MgO      | 0.08       |
| ZnO      | 0.06       |
| Cl       | 0.01       |

Figure 1. XRD pattern of synthesized TiO$_2$ powder

Figure 2(a) shows the morphology of the synthesized TiO$_2$ powder from the ilmenite concentrate. Morphology of synthesized TiO$_2$ powder was in the form of spherical granules with an average particle size of 0.53 µm. For the implementation in DSSC application, spherical structure is the most widely used because it has a high surface area so that the amount of dye absorbed would increase and allow as much light to enter the surface as possible [10]. The morphology of the synthesized TiO$_2$ powder shows that there are plenty of pores that would allow the dye to be absorbed well into TiO$_2$, as well as adsorbing
more electrolytes containing redox mediators so it could facilitate the passage of electrons easily [11]. In Figure 2(a), it can also be seen that the particles agglomerate to a larger size due to the presence of Fe deposits in TiO₂ which were evenly distributed and appeared to be homogeneous. The EDS test was conducted to determine the elemental content of the sample shown in Table 2 and Figure 2(b). The EDS result shows that the synthesized TiO₂ powder contained Fe impurities, which was likely to contribute to the yellowish color pigment observed in the synthesized TiO₂ powder.

Figure 2. (a) SEM image and (b) EDS spectrum of synthesized TiO₂ powder

Table 2. Composition of synthesized TiO₂ powder

| Element | wt % |
|---------|------|
| O       | 53.33|
| Ti      | 45.33|
| Fe      | 1.13 |
| Total   | 100  |

The value of energy bandgap of the synthesized TiO₂ powder was estimated from UV-Vis DRS characterization data using the Kubelka-Munk method as shown in Figure 3. The synthesized TiO₂ powder value had an anatase phase with an energy bandgap value of 3.0 eV, where it was smaller than most commonly reported energy bandgap value for anatase phase, i.e. 3.2 eV [4,5]. One of the possible reasons is because the synthesized TiO₂ powder did not have nano-sized granules, where the decrease in grain size would cause greater energy band gap value from the material [12]. In addition, the decrease in the band gap value of the synthesized TiO₂ was attributed the presence of Fe impurities. The increase in the amount of Fe in TiO₂ has been reported to decrease the energy bandgap value of TiO₂ [13].
Gas sorption analysis was used to determine the Brunauer-Emmett-Teller (BET) surface area of the synthesized TiO$_2$ powder. The surface area of the synthesized TiO$_2$ powder was 138.39 m$^2$/g. Surface area is an important property in DSSC application. The greater the surface area, the amount of dye absorbed would increase so that the DSSC efficiency would increase. Besides, the porosity of the synthesized TiO$_2$ powder was also calculated from the BET testing data, giving a value of approximately 0.65. Porosity also affects DSSC performance. The smaller the porosity value, the more increase the absorption coefficient of light, so that the current and voltage produced would increase. According to Ni et al, good porosity value used for DSSC is around 0.41 because when the porosity was 0.41 the maximum power value generated was greater than the others [14].

The performance of DSSC with the synthesized TiO$_2$ photoanode was compared to the performance of DSSC with commercial TiO$_2$ (Merck) photoanode. Figure 4(a) shows a graph of current density-voltage (J-V) of DSSC with a variation of the TiO$_2$ photoanode. DSSC conversion efficiency depended on the value of short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), Fill Factor (FF), and the power of incoming light ($P_{in}$). The efficiency of DSSC and Fill Factor DSSC can be calculated using Equations 1 and 2.

\[
\text{FF} = \frac{V_{\text{max}} \times J_{\text{max}}}{V_{oc} \times J_{sc}}
\]

\[
\eta = \frac{P_{\text{max}}}{P_{in}} = \frac{J_{sc} \times V_{oc} \times \text{FF}}{P_{in}} \times 100\%
\]

Table 3. Electrical parameters of DSSC with various photoanode TiO$_2$

| Photoanode       | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF  | Efficiency (%) |
|------------------|--------------|----------------------|-----|----------------|
| TiO$_2$ Merck    | 0.68         | 36.40                | 0.40| 1.99           |
| TiO$_2$ Synthesis| 0.66         | 9.60                 | 0.61| 0.75           |
Figure 4. (a) J-V curves of DSSCs and (b) IPCE spectrum of DSSCs

The graph in Figure 4 (a) shows that the performance of DSSC with the synthesized TiO$_2$ photoanode from Bangka ilmenite was lower than DSSC with Merck TiO$_2$ photoanode. DSSC with the synthesized TiO$_2$ photoanode produced conversion efficiency of 0.75%, while DSSC with Merck TiO$_2$ produced conversion efficiency of 1.99%. The plausible reason for the lower efficiency is because the synthesized TiO$_2$ powder contained Fe impurities. Although the presence of Fe impurities increased the adsorption of dye molecules, the existence of Fe also caused the TiO$_2$ granules to agglomerate so that the size became larger [9]. The DSSC parameters with various TiO$_2$ photoanode are shown in Table 3. The DSSC performance was also tested using incident photon-to-current efficiency (IPCE) to determine the value of the conversion efficiency of photons into electric currents at specific wavelengths. Figure 4 (b) shows the IPCE spectrum of DSSC with variations of the TiO$_2$ photoanode. It can be seen that most of the visible light conversion into electric by the synthesized TiO$_2$ occurred at a wavelength range of 380-700 nm. The IPCE spectrum of DSSC with Merck TiO$_2$ and the synthesized TiO$_2$ did show any significant differences. The IPCE graph also shows a sharp peak at a wavelength around 340 nm, which was related to the absorption of the energy band gap of TiO$_2$ [15]. Meanwhile, the second IPCE peak at a wavelength of about 520 nm was related to the maximum absorption of the dye. The fundamental difference between the IPCE spectra of TiO$_2$ Merck and the synthesized TiO$_2$ was the large difference in the intensity of the photon-to-current conversion. The higher the value of IPCE, the more number of photons converted to current [16]. IPCE values had increased in anatase DSSC TiO$_2$ due to high surface area and higher size than other phases of TiO$_2$, so the dye was well absorbed [17].

4. Conclusions

TiO$_2$ powder was successfully synthesized from Bangka ilmenite concentrate with a caustic fusion method having an anatase phase, a grain size of 0.53 μm, and a band gap value of 3.0 eV. DSSC with the synthesized TiO$_2$ photoanode was successfully fabricated with a layer thickness of 22 ± 0.89 µm having $J_{sc}$ 9.60 mA/cm$^2$, $V_{oc}$ 0.66 V, FF 0.61, and a conversion efficiency of 0.75%. Although the conversion efficiency of the DSSC with the synthesized TiO$_2$ photoanode is lower than the DSSC with commercial TiO$_2$ (Merck), our work demonstrated that ilmenite minerals show great potential to be applied in DSSC. The cost of fabrication of DSSC in Indonesia is expected to be significantly reduced by employing ilmenite-based TiO$_2$ as photoanode due to its abundant availability.

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