Dye-sensitized solar cells using double-oxide electrodes: a brief review

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Abstract. Dye-sensitized solar cells (DSC or DSSC) have been widely investigated because of their potentially high cost performance compared with Si-based solar cells and of their fascinating appearance. DSC with photoelectric conversion efficiency of >10 % (or even 12 %) have been reported, where porous TiO2 films are generally used as semi-conductor electrodes. Such porous TiO2 films usually have high specific surface area, and thus, they adsorb plenty of dye molecules, resulting in high photocurrent density. Recently, some double oxides have been examined as alternative photoanode materials, mainly in order to improve photovoltage. Here, studies on DSC using double-oxide electrodes, i.e., perovskite, spinel, ilmenite, wolframite, scheelite and pseudobrookite-types, are briefly reviewed.

1. Introduction

After the pioneer work on dye-sensitized solar cells (DSC or DSSC) by O’Regan and Grätzel in 1991 [1], wide variety of oxide-based semiconductors, instead of TiO2, have been studied as alternative electrode materials of DSC. Here, studies on DSC using double-oxide electrodes are briefly reviewed with focusing on the simple replacement for TiO2, i.e., double-oxide-based phase-pure porous electrode (type A in Fig. 1 [2]).

Figure 1. Non-TiO2 oxides used for DSC electrodes: (A) phase-pure porous electrode, (B) composite electrode with TiO2, and (C) coating materials on TiO2. Reproduced with permission from ref. [2]

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2. Perovskite-type oxides (ABO₃)

Among various double oxides, perovskite-type oxides have been most widely studied due to the band-structure similarity to TiO₂. In 1999, Burnside et al. [3] synthesized nanocrystalline mesoporous SrTiO₃ by hydrothermal treatment of nanocrystalline TiO₂ and Sr(OH)₂ at 190°C for 4.5 h, and applied the obtained nanocrystalline SrTiO₃ to photoanodes of DSC by sintering at 500-600°C in a flowing oxygen atmosphere. They confirmed that the dye uptake of the SrTiO₃ films was about half of the TiO₂ anatase film, which suggests that the surface treatment of SrTiO₃ or the optimization of dye may improve the cell performance.

In 2001, Lenzmann et al. [4] reported SrTiO₃ nanocrystalline photoanode, which was evaluated by surface photovoltage spectroscopy. They found a blue shift for the SrTiO₃-based cell as compared to the TiO₂ anatase based cell. In 2010, Yang et al. [5] determined the flat band edges (E₀) of nanstructured SrTiO₃ electrodes in propionitrile (PN), acetylacetone (Acac) and PN/Acac mixture. They also prepared N₃-dye sensitized SrTiO₃ and evaluated its photovoltage-photocurrent curves (Table 1). They reported short-circuit current density (Jₛ𝑐) of nanocrystalline SrTiO₃, but the power conversion efficiency (PCE) was not stated in detail.

In 2014 (online in Oct. 2013), based on the Yang's work [5], Jayabal et al. [6] pointed out that (1) both TiO₂ and SrTiO₃ have similar band gap of value of ~3.2 eV, but the flat-band potential of SrTiO₃ is greater than that of TiO₂ anatase, and (2) the conduction band of SrTiO₃ lie ~0.2 eV above the conduction band of TiO₂ anatase, hence SrTiO₃ is expected to produce excellent photovoltage. To demonstrate the feasibility of SrTiO₃, Jayabal et al. synthesized mesoporous SrTiO₃ via hydrothermal treatment of Sr(CH₃COO)₂ and Ti[OCH(CH₃)₂]₄ at 120°C for 12 h with post calcination at 900°C for 6 h, and they applied it to DSC (Table 1). High Vₒ𝑐 of 0.73 eV is ascribed to the more negative positioned conduction band of SrTiO₃, and low current density is attributed to the reverse saturation current.

Also in 2014, Okamoto et al. [2] reported the synthesis of SrTiO₃, CaTiO₃ and BaTiO₃ submicron powders by solid-state reaction at 1200°C for 2 h followed by planetary ball-milling, and they applied the powders to DSC (Table 1). Without the optimization of redox electrolyte etc., PCE values of this research were much lower than other works. Still, they succeeded to demonstrate the difference among three perovskite-type electrodes. Note that the SrTiO₃ and BaTiO₃ powders were effective as second phases of composite type electrodes (type-B in Fig. 1). In 2015 (online in Oct. 2014), Li et al. [7] synthesized Ho³⁺-doped SrTiO₃ in order to obtain the down-conversion effect and p-type doping effect. Although PCE values of their study were also much lower than other works, apparent increase in Jₛ𝑐 was confirmed. Besides titanates, other perovskite-type oxides have been also studied, such as barium stannate (BaSnO₃) with band gap of 3.1 eV[8,9]. Shin et al. reported the PCE of 4.5% for bare BaSnO₃,

| Electrode          | Electrode area (cm²) | Electrode thickness (µm) | Type of dye | Light source (mW/cm²) | Vₒ𝑐 (V) | Jₛ𝑐 (mA/cm²) | FF (%) | PCE (%) | References               |
|--------------------|----------------------|--------------------------|-------------|------------------------|----------|---------------|--------|---------|--------------------------|
| SrTiO₃             | –                    | 5-6                      | N3          | ~100                   | 0.789    | 3             | 0.70   | 1.8     | Burnside (1999) [3]       |
| SrTiO₃             | –                    | –                        | EY*         | 62.5                   | 0.73     | 0.44          | 0.55   | 0.51(?) | Jayabal (2014) [6]        |
| SrTiO₃             | 1                    | ~ 10                     | N719        | 100                    | 0.636    | 0.128         | 0.464  | 0.038   | Okamoto (2014) [2]        |
| CaTiO₃             | 1                    | ~ 10                     | N719        | 100                    | 0.488    | 0.0172        | 0.312  | 0.0026  | Okamoto (2014) [2]        |
| BaTiO₃             | 1                    | ~ 10                     | N719        | 100                    | 0.650    | 0.127         | 0.433  | 0.036   | Okamoto (2014) [2]        |
| SrTiO₃             | 0.25                 | –                        | N719        | 100                    | 0.54     | 0.15          | 0.51   | 0.04    | Li (2015) [7]             |
| Ho³⁺-doped SrTiO₃  | 0.25                 | –                        | N719        | 100                    | 0.60     | 0.23          | 0.49   | 0.07    | Li (2015) [7]             |
| BaSnO₃ (CP)        | 0.4                  | ~ 10                     | N719        | 100                    | 0.68     | 2.77          | 0.60   | 1.1     | Guo (2010) [8]            |
| BaSnO₃ (HT)        | 0.4                  | ~ 10                     | N719        | 100                    | 0.67     | 2.04          | 0.59   | 0.8     | Guo (2010) [8]            |
| BaSnO₃ (SSR)       | 0.4                  | ~ 10                     | N719        | 100                    | 0.58     | 0.37          | 0.47   | 0.1     | Guo (2010) [8]            |
| BaSnO₃             | 0.16                 | –                        | N719        | 100                    | 0.61     | 11.19         | 0.66   | 4.5     | Shin (2013) [9]           |

*EY: Eosin Yellow, CP: coprecipitation, HT: hydrothermal, SSR: solid-state reaction.
Table 2. DSC using spinel, ilmenite, wolframite, scheelite and pseudobrookite-type double oxide electrodes.

| Electrode | Electrode area (cm$^2$) | Electrode thickness (µm) | Type of dye | Light source (mW/cm$^2$) | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF | PCE | η (%) | References |
|-----------|-------------------------|--------------------------|-------------|--------------------------|--------------|----------------------|----|-----|------|------------|
| Spinel    |                         |                          |             |                          |              |                      |    |     |      |            |
| Zn$_2$SnO$_4$ | 0.20                   | 5.6                      | N719        | ~100                     | ~0.62        | ~9.1                 | ~0.67 | 3.8  |        | Tan (2007) [10] |
| Zn$_2$SnO$_4$ | 0.32                   | 5.7                      | N719        | 100                      | 0.68         | 2.4                  | 0.68  | 1.0  |        | Lana-Villarreal (2007) [11] |
| Mg$_2$TiO$_4$ | 1.0                    | 30.8                     | N719        | 100                      | 0.586        | 0.033                | 0.293 | 0.0056 |        | Ishii (2015) [12] |
| Ilmenite   |                         |                          |             |                          |              |                      |    |     |      |            |
| CdSnO$_3$  | 0.2                     | 15                       | N719        | ~100                     | 0.43         | 7.43                 | 0.45  | 1.42 |        | Natu (2010) [13] |
| MgTiO$_3$  | 1.0                     | 28.8                     | N719        | 100                      | 0.515        | 0.048                | 0.317 | 0.0079 |        | Ishii (2015) [12] |
| Wolframite |                         |                          |             |                          |              |                      |    |     |      |            |
| Zn$_2$WO$_4$ | 0.25*                   | ~12*                     | N3*         | 100                      | 0.57         | 0.21                 | 0.459 | 0.054 |        | Kim (2011) [14] |
| MgWO$_4$   | 0.25*                   | ~12*                     | N3*         | 100                      | 0.46         | 0.18                 | 0.429 | 0.036 |        | Kim (2011) [14] |
| Scheelite  |                         |                          |             |                          |              |                      |    |     |      |            |
| CaWO$_4$   | 0.25*                   | ~12*                     | N3*         | 100                      | 0.41         | 0.13                 | 0.422 | 0.023 |        | Kim (2011) [14] |
| SrWO$_4$   | 0.25*                   | ~12*                     | N3*         | 100                      | 0.39         | 0.12                 | 0.433 | 0.020 |        | Kim (2011) [14] |
| Pseudobrookite | 1.0                    | 42                       | N719        | 100                      | 0.465        | 0.060                | 0.248 | 0.0069 |        | Ishii (2015) [12] |

*Jung et al. [15]  

3. Spinel-type oxides (AB$_2$O$_4$)

Spinel-type double oxide group (general formula: AB$_2$O$_4$) also contains many compounds. Some spinel-type oxides have been examined as photoanodes of DSC. In 2007, Tan et al. [10] examined zinc stannate, Zn$_2$SnO$_4$ (inverse spinel type, Zn[Zn,Sn]O$_4$) with band gap of 3.6 eV, and reported the PCE of 3.8%. According to Tan et al., the electron diffusion length for Zn$_2$SnO$_4$ is shorter than P25 TiO$_2$ film. However, for thin films (≤ ~ 6 µm), the photocurrent density for a Zn$_2$SnO$_4$ cell was higher than that for a P25 cell with the same film thickness. Lana-Villarreal et al. [11] also reported the DSC performance of Zn$_2$SnO$_4$ DSC.

In 2015, Ishii et al. [12] reported Mg$_2$TiO$_4$ (inverse spinel type) with band gap of 3.7 eV as a photoanode of DSC. In their preliminary data, since Mg$_2$TiO$_4$ particles were large and film thickness was not optimized (too thick as a photoelectrode), DSC performance was rather low. Similar to Zn$_2$SnO$_4$, the electron diffusion length for Mg$_2$TiO$_4$ may be shorter than TiO$_2$. Further optimization will be expected.

4. Ilmenite-type oxides (ABO$_3$)

When the ionic radii of A and B ions in ABO$_3$ are similar to each other, ilmenite-type double oxides preferably form instead of perovskite-type. Some ilmenite-type oxides also have been studied as photoanodes of DSC. In 2010, Natu and Wu [13] studied cadmium stannate, CdSnO$_3$ with band gap of 3.07 eV, and reported the PCE of 1.42%. The conduction band edge of CdSnO$_3$ is ca. 0.9 eV lower than that of TiO$_2$ anatase. A merit of CdSnO$_3$ double oxide is its higher stability in an acidic environment than SnO$_2$. Ishii et al. [12] also preliminary reported on MgTiO$_3$ with band gap of 3.7 eV as a photoanode of DSC.

5. Wolframite and scheelite-type oxides (MWO$_4$)

In 2011, Kim et al. [14,15] prepared divalent metal tungstates, MWO$_4$, with wolframite (M=Zn and Mg) and scheelite (M=Ca and Sr) structures by a solid-state reaction method, and applied them for DSC. Wolframite-type showed better performance than scheelite-type, which is attributable to their enhanced electron transfer resulting from appropriate band positions. The band gaps of ZnWO$_4$, MgWO$_4$, CaWO$_4$ and SrWO$_4$ are 2.95, 3.48, 4.25 and 4.58 eV, respectively. Correspondingly, the PCE of ZnWO$_4$, MgWO$_4$, CaWO$_4$ and SrWO$_4$ were 0.054, 0.036, 0.023 and 0.020%, respectively.
6. **Pseudobrookite-type oxides (MgTiO\(_3\))**

Another double oxide in MgO-TiO\(_2\) binary system, MgTi\(_2\)O\(_5\) (pseudobrookite, band gap of 3.4 eV) was also preliminary studied by Ishii et al. [12].

7. **Conclusion**

Studies on DSC using perovskite, spinel, ilmenite, wolframite, scheelite and pseudobrookite-type double oxides are briefly reviewed. Common positive aspect using double oxide will be their flexibility of band tuning. Perovskite-type BaSnO\(_3\) and spinel-type Zn\(_2\)SnO\(_4\) are most promising to date. Compared with conventional TiO\(_2\)-based DSC, however, further optimization is required.

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