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Novel cost-effective and electrocatalytically active intermetallic nickel aluminate counter electrode for dye sensitized solar cells

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Abstract

The very high cost, scarcity and dissolubility of platinum (Pt) is the center of debates as a counter electrode (CE) in dye sensitized solar cells (DSSCs) research domain. To deal with such core issues, herein, novel low-cost and electro-catalytically active inter-metallic nickel aluminate (Ni3Al) thin films have been fabricated successfully on fluorine-doped tin oxide substrates by DC magnetron sputtering at room temperature. For the first time, Ni3Al has been utilized as a CE for DSSCs application. Further, the solar cell performance of Ni3Al based DSSC has compared with the sputtered coated Pt thin film based DSSC performance. Under open atmospheric experimental preparation conditions (in air), a maximum power conversion efficiency of 3% has been achieved with Ni3Al CE. The obtained efficiency is quite analogous to a DSSC fabricated with a Pt CE. Further, as-fabricated Ni3Al CEs have exhibited better electrochemical catalytic activity and anti-corrosion effect than that of sputtered Pt CEs. The low-cost and excellent electrocatalytic properties of intermetallic Ni3Al thin films may pave the way towards development of Pt-free CE for DSSCs.

1. Introduction

DSSC is one of the alternatives for Si and thin film based solar cells due to their ability to work under diffused light conditions, ease of fabrication and economically affordable processes [1, 2]. To strengthen the competitiveness of DSSC in the area of solar cell, it is imperative to further improve the power conversion efficiency (PCE), performance stability for a longer period and reduction of the device cost. DSSC is mainly composed of a wide band-gap n-type semiconductor material (photoanode), sensitizer (organic/inorganic dye molecules), an electrolyte containing an iodide/tri-iodide (I−/I3−) redox shuttle and a counter electrode (CE). The CE is an essential component of DSSCs, which plays crucial role in collecting electrons from the outer circuit and catalyzing I3− through reduction process to afford I−, responsible for the re-oxidation of dyes [3]. An ideal CE should possess high conductivity and catalytic activity with better chemical stability. Currently, in most of the DSSCs devices platinum (Pt) coated glass is used as a standard CE due to its high catalytic activity and excellent electrical conductivity. However, high cost of the Pt and its lack of availability could hinder the mass production of DSSCs [4-7]. Similarly, several research groups have already reported corrosion/deterioration studies of Pt CE in the presence of I−/I3− during the photovoltaic (PV) process [8]. To overcome such critical issues, various materials have been explored as potential alternatives to Pt, including carbon, metal oxides, transition metal sulfides, nitrides, and carbides [9-14]. Recently, C Wu and et al have demonstrated compound of carbon and nitrogen that forms carbon nitride as a Pt-free electrode for DSSC, and showed maximum 4.45% PCE [11]. For the high PCE of the solar cell, these CE materials should possess better electro-catalytic property with long term stability. The materials which are possessing both properties (high conductivity/high catalytic activity) along with low cost material may be a game changer in the area of DSSC. Many intermetallic alloys show
such useful properties for DSSC applications [15–17]. Intermetalics are consisting of two or more metal and non-metal atoms, which are generally exists in solid compound. Usually, conventional alloys are bonded with relatively weak metallic bonds, whereas, ordered intermetalics possesses strong ionic and covalent bond in a crystalline manner. These structured characteristics are responsible to have excellent physical, electrical and mechanical properties. For example, high melting point, improved electrical conductivity, anti-corrosive properties and high strength, and etc. In the present work, for the first time, DC magnetron sputtered Ni3Al thin films demonstrating the utility as a CE in DSSC. Ni3Al is an ordered intermetalic material, revealed many attractive properties including high melting point and mechanical strength, excellent oxidation/corrosion resistance, low-density, good thermal and electrical conductivity [18–20]. Among these properties, good corrosion resistance and high electrical conductivity have been stimulated to develop Ni3Al as a CE material in PV devices.

2. Experimental details

2.1. Fabrication of Ni3Al and Pt counter electrode

Nano crystalline Ni3Al and Pt thin films were fabricated on cleaned FTO substrates using Ni3Al (75%Ni and 25%Al) and pure Pt (99.9%) metal discs. Thin film depositions have been performed by ultra-high vacuum magnetron sputtering system at room temperature. All sputtering parameters (viz. time, flow rate, power, pressure etc) were optimized to get uniform thickness and crystalline nature of Ni3Al and Pt. (The optimized parameters:- Gas = Ar, Flow rate = 4 sccm, Power = 150 W, Base pressure = 10-6 mbar, Deposition time = 5 min). Prior to deposition of thin films, FTO substrate has subjected to standard cleaning procedure including gently rub with detergent followed by sonication for 10 min each in distil water, isopropyl alcohol. Finally all the substrates were dried with hot air-gun.

2.2. Device fabrication

In order to fabricate TiO2 photoanode, first, TiO2 powder has synthesized with DC arc plasma method in oxygen atmosphere. Further, photoanode have deposited by electrophoretic technique as details given in elsewhere [21]. Subsequently, FTO/TiO2 thin film has immersed in Ruthenium (N719) dye for 24 hours, which was freshly prepared in ethanol (dye concentration = 0.5 mM). The DSSC was assembled using sensitized photo-anode and CE. For redox reaction, \( I^- / I_3^+ \) redox couple was prepared by combination of \( I_2, LiI \) and tert-butylpyridine in acetonitrile (5 mM), used as electrolyte. Plastic tape was stuck on four sides of the photo electrode and Ni3Al and Pt CE, and placed on top. Electrolyte was injected through edges of CE to spread over the device active area (1 × 1 cm²). Assembly and electrical measurement of DSSC were performed at room temperature in open atmospheric (without glove box) condition.

2.3. Characterization of DSSC components

The crystallinity of Ni3Al and Pt thin films were analyzed using Bruker-D8 Discover x-ray diffractometer. The morphology of thin films were analyzed by FESEM(ZEISS) at 5 kV with 50 kX magnification. The performance of fabricated cells were analyzed under solar simulator (Oriel, USA) at 100 mW cm⁻² (AM.1.5 G) intensity; while current density-voltage (J-V) characteristics were measured using Keithley-2420. Electrochemical measurements of both CEs were performed using electrochemical workstation CHI660E. The Cyclic voltammetry (C-V) analyses were performed at −0.2 to 0.8 V with 50 mV s⁻¹ scan rate throughout experiments using three electrode systems. Ag/Ag⁺ used as a reference electrode for the C-V measurements. EIS measurement was carried out under the dark condition at frequency range of 1 Hz–1 MHz, 0.005 V amplitude, and 0.7 V applied potential (Equivalent to Voc of the DSSC).

3. Results and discussions

3.1. Structural and morphological analysis

Figures 1(a), (b) shows XRD pattern of Ni3Al and Pt thin films on FTO substrates, where the diffraction patterns are dominated from FTO substrates. The XRD pattern have seen only two (111), (220) peaks at 43.98°, 51.52° are indexed to the Ni3Al phase (JCPDS 65-3245) and three (111), (200), (220) peaks at 38.68°, 44.97°, 65.48° are indexed to Pt phase (JCPDS 87-0644) respectively. These observations are clearly indicating a thin crystalline layer of Ni3Al/Pt has been formed on the FTO substrate without other impurity phase. The XRD pattern depicts Ni3Al/Pt signature peak along with FTO, since thin films were deposited on FTO substrate.

FESEM micrographs of Ni3Al and Pt thin films exhibit profound large grains with orientations as shown in figure 2. This morphology is due to the high sputtering power (Ni3Al/Pt~150 W), which helps to increase the surface mobility of adatoms, and form uniform crystalline film. In the sputtered deposition, homogeneity was
maintained in both Ni3Al and Pt thin films. Further, EDX spectra of Ni3Al and Pt are shown in lower portion of figure 2. The EDX spectrum of Ni3Al thin films deposited at 150 W, demonstrate the presence of Ni (∼73.96%) and Al (∼26.04%) with approximately 3:1 chemical composition. These compositions were observed accurately in the deposited film. Similarly, Pt elements were seen in the pure form from EDX spectra. One can observe that, there are no foreign elements present in Ni3Al and Pt except Sn owing to the FTO substrate. Therefore, quantity of unnamed peak belongs to Sn, and has reduced from the calculations.

3.2. Photovoltaic performances of the cells

J-V measurements have been performed on cell active area of 1 × 1 cm² and summarized their results in inset of figure 3(a). The Ni3Al CE based DSSC exhibited 7.2 mAcms⁻² photocurrent density (Jsc), and 0.73 V open circuit voltage (Voc). Further, fill factor and efficiency of the device have been calculated as 0.59 and 3.0 % respectively. For better device comparison, Pt CE employed DSSC, which illustrates Jsc of 7.7 mAcms⁻² and Voc is 0.77 V with improved efficiency (3.3%). The Pt-based device shows bit higher PCE than Ni3Al-based device. However, the generated photocurrent by both devices is almost equivalent. The PCE of the Pt CE based DSSC shows bit lower
than many DSSCs reported elsewhere \cite{9, 11}. The probable reason could be the device fabrication condition and active area of the device ($1 \times 1$ cm$^2$). In brief, the DSSC were fabricated at room temperature in open atmospheric (without glove box, i.e. No inert atmosphere). Due to open atmosphere, very fine or micro particles may induced in the thin films which may act as a recombination centers and leading to degrade the performance of the devices. Similarly, as the device size increases, the chances of carrier recombination are more, which further affects the overall PCE of the DSSC. The experimental observations of DSSCs are suggesting to utilize Ni$_3$Al CE as a replacement of Pt in DSSC.

**Figure 3.** (a) J-V measurement of DSSCs (cell active area of $1 \times 1$ cm$^2$) based on Pt and Ni$_3$Al CEs; (b) Cyclic voltammetry analysis of Ni$_3$Al and Pt CEs; and (c) Nyquist plots of sputtered coated Pt and Ni$_3$Al CEs.
3.3. Electrochemical properties of CEs

The cyclic-voltammetry (CV) measurement is one of the most useful tools to study the electrochemical reactions of CEs. In this work, CV measurements were conducted in a three-electrode system at –0.2 to 0.8 V potential windows with 50 mV s\(^{-1}\) scan rate in the I\(^3\)/I\(^-\) electrolyte. The comparative electro-catalytic activities of Pt and Ni\(_3\)Al CEs are shown in figure 3(b). One can see the pair of reductive and oxidative peaks at respective potential for Ni\(_3\)Al and Pt electrodes designated in the figure 3(b). These values are depicting the redox reaction of I\(^3\) \(\rightarrow\) I\(^-\) (Red: I\(^{3+}\) + 2e\(^-\) \(\leftrightarrow\) 3I\(^-\) and Ox: 3I\(^-\) 2e\(^-\) \(\leftrightarrow\) I\(^3\) ) at the CE and I\(^3\)/I\(^-\) couple interfaces. During the photovoltaic measurement, leaching of Pt in electrolyte was observed. This behavior might be due to the corrosion/decomposition of Pt in iodide containing electrolytes to generate PtI\(_4\) [22, 23]. However, Ni\(_3\)Al doesn’t show such leaching behavior in the given electrolyte. The photographs of Pt and Ni\(_3\)Al electrodes have shown in inset of figure 3(c) reveal leaching effect from the working area of device. For further confirmation of their electrochemical behavior and their kinetics has been carried out through EIS measurements. This technique confirms charge transfer processes at CE interfaces. To clear the picture of electrodes leaching, Ni\(_3\)Al and Pt electrodes were kept for 60 min in electrolyte solution, and prepared four samples, i.e. Pt, Ni\(_3\)Al, Pt\(_{60\ min}\), and Ni\(_3\)Al\(_{60\ min}\) (Pt/Ni\(_3\)Al film immersed in the electrolyte solution for 60 min). EIS measurement have been performed by two electrodes systems, i.e. Pt foil as a counter and sputtering deposited Pt/Ni\(_3\)Al film as a working electrode. All Nyquist plots of specified samples have been fitted using Z-view software and their analyzed interfacial resistances and their respective capacitances have been illustrated in table 1. Inset of figure 3(c) shows equivalent circuit, representing ohmic resistance and non-ideal capacitive behavior at interfaces, where \(R_0\) = series resistance/substrate resistance, \(R_1\) = charge transfer resistance at electrolyte/anode interface; \(R_2\) = electron diffusion in cathode electrode interfaces. This EIS measurement forms an electrochemical cell stack which involve two electrodes, i.e. working electrode and CEs, therefore, we obtained two semicircles at the higher and lower frequency range of the Nyquist plot [24, 25]. A small semi-circle in high frequency zone and large semi-circle in lower frequency region can be seen in the figure 3(c). Before PV measurement, Pt CE shows less resistances of \(R_1\) (20.6 \(\Omega\)) and \(R_2\) (34.8 \(\Omega\)). However, after keeping Pt electrode for 60 min in I\(^3\)/I\(^-\) electrolyte, \(R_1\) and \(R_2\) of Pt increased to 65.7 and 205 \(\Omega\) respectively. The change in resistances indicates the leaching of Pt. Similarly, neat Ni\(_3\)Al film clearly indicates identical resistances of \(R_1\) and \(R_2\) (~33 \(\Omega\)). Whereas, Ni\(_3\)Al\(_{60\ min}\) sample demonstrates change in resistance of \(R_1\) and \(R_2\) are 37.2 and 51.1 \(\Omega\) respectively. This shows very less leaching effect as compare to Pt CE. Importantly, electron diffusion resistance (\(R_2\)) of Ni\(_3\)Al\(_{60\ min}\) is ~4 times lesser than Pt\(_{60\ min}\) electrode. In addition, sheet and charge transfer resistance of Pt CE also observed very less (5 \(\Omega\) and 20.6\(\Omega\)) as compared to Ni\(_3\)Al CE, which may be responsible for efficiency enhancement in Pt CE based DSSC. Therefore, we can judge that, as prepared Pt CE provides comparatively better performance than Ni\(_3\)Al CE; however, Ni\(_3\)Al\(_{60\ min}\) samples show better stability than Pt CE. This result demonstrates the better electrocatalytic activity of Ni\(_3\)Al electrode than that of Pt CE for I\(^3\)/I\(^-\) redox reaction. It has been proved that the nanostructured Ni\(_3\)Al CE is a good candidate for Pt-free DSSCs, with better charge-transfer stability in electrolyte.

| Samples       | \(R_s\) (\(\Omega\)) | \(R_1\) (\(\Omega\)) | \(R_2\) (\(\Omega\)) | \(R_{total}\) (\(\Omega\)) | \(C_1\) (\(\mu\)F) | \(C_2\) (\(\mu\)F) |
|---------------|---------------------|---------------------|---------------------|---------------------------|-----------------|-----------------|
| Pt            | 5                   | 20.6                | 34.8                | 60.4                      | 8.53            | 0.046           |
| Pt\(_{60\ min}\)| 5.7                 | 56.7                | 205                 | 267.4                     | 2.25            | 0.012           |
| Ni\(_3\)Al    | 6.25                | 33                  | 33.5                | 72.75                     | 0.018           | 0.005           |
| Ni\(_3\)Al\(_{60\ min}\)| 6.5                 | 37.2                | 51.1                | 94.8                      | 0.016           | 0.012           |

4. Conclusions

Ni\(_3\)Al and Pt thin films have been successfully deposited and analyzed with XRD, FESEM and EDX. Further, DSSCs (cell active area of 1 \(\times\) 1 cm\(^2\)) have been fabricated with Pt/Ni\(_3\)Al CEs, and tested under similar experimental conditions. The Ni\(_3\)Al CE based DSSCs have comparable PCE (3%) with typical sputtered Pt catalyzed cells. Electrocatalytic activity depicts comparable in-fact better results than the Pt. Cost-effective Ni\(_3\)Al CE also showed good stability in commonly used I\(^3\)/I\(^-\) electrolyte than Pt CE. The low-cost and chemically stable Ni\(_3\)Al film stands out as an alternative CE for new generation photovoltaic devices.
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