Anodized aluminum–silicon alloy counter electrode substrates for next generation solar cell applications

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A B S T R A C T

Aluminum–silicon (Al–Si) alloy based counter electrode substrates were developed for next generation solar cells. Controlled anodization was performed on the Al–Si alloys to form an aluminum oxide (AO) with corrosion resistant microstructure. Presence of secondary Si particles in the Al–Si alloy system facilitated electrical conduction across the insulating AO film. In this way, aluminum is rendered suitable as substrate for photovoltaic applications without having to resort to its coating with costly conductive metals such as titanium. Current density–voltage (J–V) measurements of dye-sensitized solar cells (DSSCs) based on the new Al–Si alloys yielded a high power conversion efficiency (η) of up to 6.13% under 1 Sun illumination condition, essentially matching the conversion efficiency, $\eta = 6.7\%$, of a reference DSSC with fluorine-doped tin oxide (FTO) glass based electrode substrates. The microstructure of the Al–Si alloys and the anodized oxide films was studied in detail by FE-SEM and XPS and correlated to the device performance. Differences between the photovoltaic characteristics of the cells were analyzed further by electrochemical impedance spectroscopy and optical reflectance spectroscopy measurements.

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1. Introduction

Energy consumption in the world is increasing drastically every year due to rapid population growth. As a result of this, there is an urgent need to integrate cost-effective technologies with renewable energy sources to achieve a sustainable environment for future generations. Solar power is promising, since it is the most abundant, clean energy resource. In order to convert solar power to electricity, photovoltaic (PV) devices are in use. Currently, silicon (Si) based PV systems dominate the PV market with relatively high efficiencies, but they suffer from high cost and heavy green-house gas emission footprint during manufacturing. Thus, researchers are looking into alternative PV technologies, which promote the use of more abundant and lower cost materials. In this context, next generation solar cells, such as organic PVs [1], dye sensitized solar cells (DSSCs) [2,3], quantum dot (QD) solar cells [4,5], and most recently perovskite solar cells [6] attract tremendous research interest. Mesoporous DSSC electrodes can be seen as a starting point of research for solid-state DSSCs [7], perovskite solar cells and even QDs, which

have led to exciting efficiency improvements within the past few years time.

Dye sensitized solar cells were first demonstrated by O'Regan and Grätzel in 1991 [8]. The mechanism for the generation of electricity in DSSCs is already explained in previous studies [2,8]. DSSCs are mainly comprised of four main components: the photoanode with titanium dioxide (TiO$_2$) layer, the dye/sensitizer, the electrolyte and the counter electrode. The counter electrode substrate, which is the focus of this research, is responsible of returning the electrons from the external load back into the circuit in the cell [9]. Counter electrode substrates are coated with a thin layer of catalyst to achieve efficient charge transfer. Platinum (Pt) is considered as one of the well-known and most widely used catalysts [10] although a number of alternative catalysts made of carbon (CNT, graphene, etc.) [11–13] or metal chalcogenides (like CoS, CuS) [14] appear to provide significant cost advantages.

As mentioned above, utilizing low cost and abundant materials along the employment of scalable, continuous processing techniques provides a great commercialization potential for these novel solar cell technologies. Transparent conductive oxide, which is generally fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO) coated glass, is widely used as an electrode substrate for solar cells. Replacing the traditionally used expensive [15], heavy, rigid

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and brittle glass electrode substrates with cheaper, lighter, flexible/bendable metals [9,16–25], plastics [22,26,27] or even mixture of both metals and plastics [28] has been one of the ongoing fields of research in solar cells.

Aluminum (Al) is already used or proposed as a substrate material for organic PVs [29] and some thin film solar cells (ex: CIGS) [30,31]. It is available in large quantities, low cost, lightweight and can be made colored. Aluminum is also capable of fulfilling some specific requirements within the PV system such as thermal stability, chemical inertness, and surface properties of a substrate material, which makes Al an ideal material to be used in building-integrated photovoltaics (BIPVs). Fabrication of solar cells on aluminum substrates will also decrease production costs, by roll-to-roll manufacturing. Significant research has been carried out previously on metal substrates and electrodes with titanium and steel proving the most promising [21,24,32]. Aluminum has also been studied as an electrode substrate for DSSC applications, but its lack of corrosion resistance was reported as the main challenge to overcome [21,33,34].

For aluminum to become suitable substrate it must be both corrosion resistant and conductive. Anodization, i.e. building an alumina layer on the metal surface may provide corrosion protection but the oxide is an insulator. The insulating nature of surface aluminum oxide has been proposed to be overcome via the deposition of a conductive coating like sputtered titanium [35] as also done with steel [36]. However, as mentioned earlier Ti constitutes an expensive material for large scale and wide application. This puzzle is solved in this work by selecting an Al–Si alloy that upon controlled anodization becomes corrosion resistant and conductive. In particular, anodized Al–Si cast alloys [37], were fabricated and demonstrated successfully as a counter electrode substrate for DSSCs. Al–Si cast alloys comprise more than 90% of all Al castings due to their excellent castability and good mechanical properties. They are used in transportation industry, building parts, portable devices and many other applications [38] hence they offer an abundant material source if properly engineered to meet the PV device requirements. To this end via anodization [39] a corrosion-resistant aluminum oxide (AO) film is formed on the Al alloy and electrical conduction is provided via embedded silicon particles present in the original Al–Si cast alloy. By careful microstructural characterization of different composition Al–Si alloys and anodization parameter optimization, highly performing DSSC counter electrodes were engineered. The novel structure of the DSSCs developed in this research can be summarized as glass/FTO/TiO$_2$/dye/electrolyte/Pt/modified AO/Al–Si alloy.

2. Experimental methods

2.1. Preparation of counter electrode substrates

Aluminum–silicon alloy based counter electrode substrates with different chemical compositions were compared with the standard FTO glass based substrates. Specimens with eight different compositions, pure Al (99.9 wt.%) and Al with 1, 2, 3.5, 5, 7, 10 and 15 wt.% Si were fabricated using permanent mold casting (ASTM B108). The specimens were prepared by melting of high purity Al and Si using electric furnace in air and were casted into a pre-heated graphite mold at 250 °C to ease the flow of the melt and also reduce possible thermal damage to the alloy. Solidified specimens were cut to 20 mm × 50 mm, having approximately 5 mm thickness. Each specimen was mechanically ground and polished with diamond suspension (up to 1 μm) to have a smooth surface finish for the anodization process. The microstructures of the cast Al–Si alloys were analyzed using a

Nikon light optical microscope with a Clemex Vision Image Analysis System.

Direct current (DC) power supply (Matsusada 120-10) was used for oxalic acid bath (OA: H$_2$C$_2$O$_4$) anodization [39]. Before anodizing, specimens were etched in sodium hydroxide (NaOH) solution (10 wt.%) at 55–60 °C for 30 s to remove the native oxide, and they were dipped in nitric acid (HNO$_3$) solution (10 wt.%) at room temperature for 30 s to desmut the surface. Specimens were rinsed with deionized water and ethanol after each step and dried under compressed air. Anodization was performed in 0.3 M OA bath at 20 °C. Aluminum plate was used as a cathode. Each specimen was anodized at constant voltage of 40 V for 5 min. Parameters such as concentration and temperature of the electrolyte, and anodization voltage were presented in previous studies [39]. The anodization duration was determined based on the optimum AO film thickness with respect to the silicon particle size distribution on the surface of Al–Si alloys, which is explained further in the results and discussion part of the paper. The surface morphologies of anodized Al–Si alloys were observed and analyzed using cold field emission scanning electron microscope (FE-SEM), Hitachi SU-8230 with energy dispersive X-ray (EDX) analysis. Chemical states of the elements on the surface of Al–Si alloys were analyzed by using X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out with a Thermo Scientific K-alpha instrument equipped with Avantage analytical software. Al-Kα radiation at 1486.6 eV was used to perform the measures. After anodization the counter electrode substrates were subjected to platinization. Few drops of 5 mM H$_2$PtCl$_6$–isopropanol solution was thermally deposited on the anodized surface of the Al–Si alloys and the FTO glass substrates at 450 °C for 30 min [10].

2.2. Preparation of photoanodes

FTO glass (from Sigma–Aldrich) with surface resistivity of ~7 Ω/sq and transmittance of 80–82% (visible) was used as a current collector part of photoanodes. Each photoanode was paired with a different type of counter electrode substrate. Holes were drilled on the FTO glass, to be able to inject electrolyte into the DSSC. Each FTO glass was cleaned in a micro-90 soap using an ultrasonic bath for 15 min. They were rinsed with distilled water and ethanol and dried under compressed air.

Titanium tetrachloride (TiCl$_4$) pre-treatment was applied prior to TiO$_2$ paste deposition to improve the cell efficiency by increasing the adhesion and mechanical strength of the nanocrystalline TiO$_2$/FTO glass interface [40]. Each photoanode was immersed in 50 mM TiCl$_4$ solution at 75 °C for 30 min. Photoanodes were sintered at 450 °C for 30 min. Commercially available TiO$_2$ paste (Dyesol 18-NRT) with ≈20 nm particle size was applied on the conductive side of each FTO glass by using the doctor blading technique [8,41]. Photoanodes were sintered at 450 °C for 30 min by using a similar sintering profile as reported previously [42]. TiO$_2$ film thickness was measured by using a surface profilometer (Dektak 3030 from Veeco Instruments Inc. U.S.A.). The film thicknesses for each cell were in the range of 8–15 μm for reliable conversion efficiency comparisons [24,40]. TiCl$_4$ treatment was reapplied as described above, in order to increase the dye loading of the TiO$_2$ film by improving inter-particle connections as described previously in the literature [43,44]. After the TiCl$_4$ post-treatment, each photoanode was immersed in 0.5 mM cis-di(thiocyanato)-N-N′-bis(2,2′-bipyridyl-4-carboxylic acid-4′-tetrabutylammonium carboxylate) ruthenium (II) (N-719) dye (from Dyesol) solution in ethanol at room temperature for 48 h and subsequently rinsed thoroughly with ethanol to remove excess physisorbed dye molecules [45,46] and dried in air.