



Improving catalyst stability in nano-structured solar and fuel cells



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ABSTRACT

Catalyst stability in nano-structured dye solar cells (DSC) and nano-composite fuel cells (NFC) is one of the most important factor that determine the lifetime of these devices. Improving catalyst stability requires strong adhesion of catalyst material on the electrode which should be chemically inert to corrosive electrolyte. In DSC, the stability of catalyst depends greatly on the catalyst deposition method. For instance, thermally platinized counter-electrodes have demonstrated long term stability at 80 °C. Whereas platinum catalyst deposited through other deposition methods such as sputtering, spin coating, chemical deposition, and electrochemical deposition, have been reported to be stable only at lower temperatures. Cheaper carbon-based catalyst materials including carbon composite structures, carbon nanotubes and graphene, have demonstrated long term stability at 60 °C during light soaking test. In NFCs, several degradation mechanisms have been reported for low temperature (LT), intermediate temperature (IT) and high temperature (HT) NFCs. New composite materials are rapidly developing as stable options for these types of NFCs. This work highlights the major developments in the catalyst stability in DSCs and NFCs.

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1. Introduction

With the continuous development of nanostructured materials, a spectacular advancement in electronic and energy devices has been reported [1–7]. Especially, energy devices including solar cells, fuel cells and charge storage devices have been undergoing significant improvement in performance utilizing numerous low-cost and novel nano-structured materials [8–12]. Nevertheless, in order to provide a sustainable energy solution, these emerging energy devices must attain long term stability to ensure successful commercialization.

Nano-structured dye solar cells (DSC) are emerging as a potential low-cost photovoltaic (PV) technology with an efficiency of 13% [13]. However, one of the major challenges which hinder their commercialization is the degradation of performance during long-term operation [14]. Similarly, different kinds of nano-composite fuel cells (NFC) are constantly developing as a potential low-cost electricity generation source [15–18]. Attaining long-term stability for these devices is crucial for their commercialization. There have been several degradation mechanisms reported in NFC which resulted in their failure for long-term operation [19–21]. Both DSCs

and NFCs devices utilizes catalyst materials for efficient performance.

In this work, the key degradation mechanisms associated with the catalyst materials in DSC and NFC are highlighted. Various organic and inorganic catalyst materials and their deposition methods reported in the literature for their use in DSC and NFC are reviewed and recommendations are suggested to improve their stability in these devices.

2. Overview of advanced catalytic materials in nano-structured dye solar cells and nano-composite fuel cells

The primary function of a catalyst material is to accelerate certain reactions without chemically reacting or physically displacing from the electrodes. Various types of catalyst materials have been used in DSCs and NFCs. The price, performance and stability of these catalyst materials determine their acceptance for commercial use in these devices. In this section, we briefly explain the functioning of DSCs and NFCs, and the catalyst materials used in these devices.

DSC consists of a meso-porous dye sensitized semiconductor film, redox hole transport materials (HTM) and catalyst material sandwiched between the conducting substrates (Fig. 1). When light falls on the DSC, the dye absorbs the light and transform into the excited state as a result of electron transfer from HOMO to LUMO level. The excited dye attains oxidized state by injecting an

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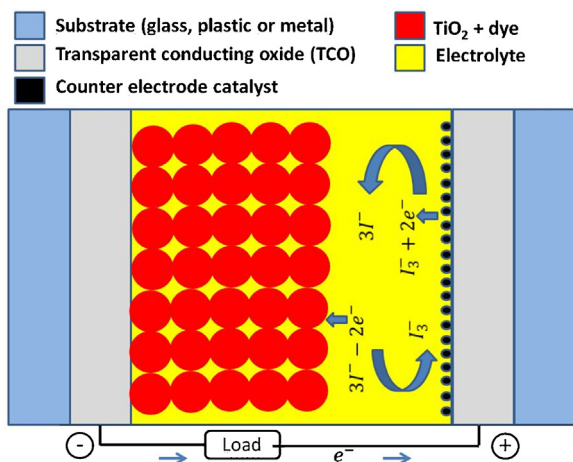


Fig. 1. Schematic structure of nano-structured dye solar cells.

electron into the conduction band of semiconductor. The electron is transported through the meso-porous semiconductor film to the conducting substrate and further reaches the counter-electrode (CE) through the external circuit. The oxidized dye is regenerated by redox HTM, which is reduced at the CE with the help of appropriate catalyst material.

The catalyst material needs to fulfill certain requirements. First, it should have excellent catalytic activity for reducing the redox electrolyte (most common electrolyte is based on an iodide/triiodide redox couple). Furthermore, it should have high conductivity for efficient electron transfer, high chemical stability against the corrosive electrolyte and strong adhesion to the electrode substrate. Finally, their cost has to be low to ensure DSCs as low-cost PV technology.

Platinum (Pt) is the most commonly used catalyst material because of its excellent catalytic activity and inert chemical nature [22–26]. Different methods have been used to deposit Pt onto the CE substrate including thermally platinized [22–24], sputtering [22–24,26], chemical deposition [22,28–30], electrochemical deposition [22,30–35], spin coating [22,36,37], dip coating [22,38,39], screen printing [40,41] and spray coating utilizing electrostatic inkjet printing [42]. These deposition methods have some advantages and limitations. The sputtering method is suitable when low temperature process is needed with high reproducibility and reasonable adhesion. However, sputtering method requires vacuum processing which is cost inefficient and slow. Chemical and electrochemical deposition methods are wet processes and are suitable for low temperature processing [30]. Although thermal platinization is the most commonly used method to prepare glass based CEs in DSCs. However, this method is not suitable when low temperature processing is required, e.g. using polymer as CE substrates. It was found that deposition method affects the performance of the Pt catalyst on CE substrate [22–41]. One of the prominent advantages of using Pt catalyst is that it makes it possible to achieve semi-transparent DSCs. However, the high cost of Pt is the limiting factor for their large scale use as catalyst material for DSCs [43]. As an alternative cheaper catalyst material, carbonaceous materials have been used at the CE of DSCs in different forms including carbon black nanoparticles [44–46], activated carbon [47–50], nanofibers [51], single wall and multiwall nano-tubes [52–55], graphene [56,57] and reduced graphene oxides [58–60]. The most common methods to deposit carbon are electrochemical [60], electrophoretic deposition [61,62], screen printing of carbon pastes [63] and spray coating [50,64]. Carbon inks are suitable for printing techniques such as spray [65,66], spin coating [67,68], dip coating [69,70], drop casting [71,72] and polymerization [73]. Excellent

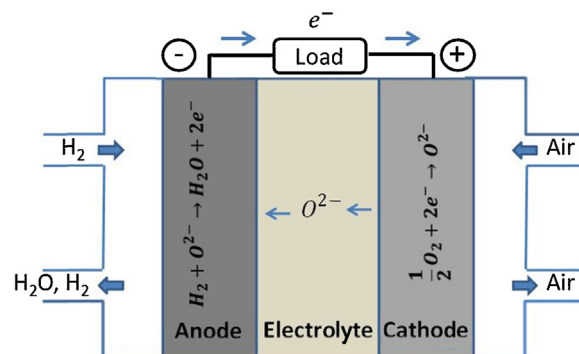


Fig. 2. Schematic structure of nano-composite solid oxide fuel cells.

catalytic performances have been achieved using carbonaceous CEs [60,74]. The catalytic performance of graphene was improved by tuning the material by increasing the amount of oxygen-containing functional groups [57]. One disadvantage of using carbonaceous CEs is compromising on the transparency of the DSCs. Another alternative organic catalyst material that has been used in DSCs is PEDOT [43]. Excellent catalytic performances have been achieved using PEDOT as CE catalyst material using different deposition methods including spin coating [67], chemically polymerization [75], electrochemical polymerization [76], spin casting followed by polymerization [77] and pulse potentiostatic electropolymerization [78]. Furthermore, PEDOT composites with other polymer materials, carbon composite materials, metal composite materials, metal oxide composite materials, metal nitrides and carbides composite materials have been used as CE catalyst materials in DSCs [43]. The main advantage of low-cost PEDOT based CEs includes possibility to achieve semi-transparency unlike in carbonaceous CEs. Composite metal sulfides [79–81], metal carbides [82,83], metal oxides [83], metal nitrides [83,84] and metal selenides [85] have also been used as CE catalyst and shown excellent catalytic performance and thermal stability. However, generally their conductivity is low because of abundant grain boundaries and defects [86]. In an effort to improve the conductivities of catalyst materials with improved catalytic activity, hybrid materials such as NiS₂/reduced graphene oxide [87], CoS/multiwall carbon nanotubes [88], TiN/carbon nanotubes [89] have been introduced. To further boost the synergistic effect in the hybrid materials, core-shell structured catalyst materials such as core-shell nitrogen doped graphene/cobalt sulfide have been reported with improved catalytic performance [90].

Like DSC, NFC is an enabling clean energy technology. An NFC is primarily consists of a cathode (+ electrode), anode (– electrode) and an electrolyte separating the two electrodes. Usually, fuels such as hydrogen, are fed from the anode side and oxygen/air is fed from the cathode side. Redox reactions occur at the anode and cathode side, whereas in electrolyte charge carriers are transported. NFCs are usually classified according to their operating temperatures and the fuels used in the operation. Low temperature FCs includes polymer electrolyte membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC) and molten carbonate fuel cell (MCFC). Solid oxide fuel cells (SOFC) operate at higher temperatures and are further classified as high temperature HT-SOFC, i.e. above 750 °C, intermediate temperature IT-SOFC i.e. between 600–750 °C and low temperature LT-SOFC i.e. below 600 °C. A schematic structure of nanocomposite SOFC is shown in Fig. 2. Recently, a novel single component nano-composite SOFC has been introduced where the three components, i.e. anode, cathode and electrolyte are mixed to form a single homogenous mixture of the three components [91,92]. The catalyst materials in NFCs play a major role in the efficient device operation.

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