

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem



Synthesis and electrochemical properties of potassium 5-trifluoromethyl-1,3,4-thiadiazole-2-thiolate/disulfide redox couple



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ARTICLE INFO

Article history: Received 3 September 2016 Received in revised form 16 December 2016 Accepted 2 January 2017 Available online 3 January 2017

Keywords: 5-Trifluoromethyl-1,3,4-thiadiazole-2-thiolate Disulfide Redox couple EMITFSI-based electrolyte Cyclic voltammetry ITO-CoS

ABSTRACT

A new redox couple, composed of the reduced species potassium 5-trifluoromethyl-1,3,4-thiadiazole-2-thiolate **2** and the oxidized species 5,5'-bis (2-trifluoromethyl-1,3,4-thidiazole) disulfide **3**, was synthesized and characterized chemically and electrochemically when dissolved in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMITFSI). Platinum (Pt), glassy carbon (GC) and cobalt sulfide-coated indium tin oxide glass (ITO-CoS) electrodes were used. The diffusion-controlled redox processes were shown to be electrochemically irreversible. At higher electrolyte temperature, the current densities are enhanced, and the potential difference between the anodic and cathodic peaks is decreased, in conjunction with a decrease in the viscosity of the electrolytic medium. The best electrocatalytic performance was obtained with the ITO-CoS electrode confirmed the very good electrochemical and mechanical stability of this electrode considered as a serious candidate to replace platinum as the counter electrode in dye-sensitized solar cells (DSSCs). The electrolytic media studied in this work exhibits a very low absorption of visible light, contrarily to the conventional I_3^-/I^- mediator, offering the possibility of illumination of the device via the counter electrode.

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1. Introduction

Solar energy is a clean, free and renewable energy that must, however, be harvested and converted. One possibility is to convert directly solar energy into electricity by using a dye-sensitized solar cell (DSSC), which has been developed by Grätzel and his team in 1991 [1]. This type of cell uses a wide band gap *n*-type semiconductor, such as TiO_2 (3.2 eV for the anatase phase). To increase the visible light absorptivity of the mesoporous material, one monolayer of dye molecules, generally consisting of a ruthenium complex, are adsorbed onto the surface of the TiO_2 particles. Upon illumination, electrons of the dye molecules are promoted from their ground state S to an excited state S^{*}. Subsequently, a very fast charge transfer (10^{-15} s) occurs between the excited state and the conduction band of TiO₂, leaving the dye in its oxidized state $(S^* \rightarrow S^+ + e^-)$. Dye molecules are regenerated by electron transfer from the reduced species of a redox couple (mediator), generally the I^-/I_3^- couple: $3I^- + 2S^+ \rightarrow I_3^- + 2S$. The electrons injected into the TiO₂ conduction band reach the external circuit, via an ohmic contact, to the counter electrode where they reduce the oxidized species of the redox couple (I_3^-) to regenerate the reduced species (I^-) .

DSSCs suffer from several drawbacks. First, oxidized species might be reduced by the electrons injected into the TiO₂ conduction band (back reaction process) [2]. Second, dye molecules may degrade under sustained illumination conditions [3]. Third, the l_3^-/l^- redox couple may react with the platinum counter electrode (to form PtI₄) [4] and corrode silver electrical contacts [5]. This redox couple has a reddish dark brown color, which is responsible for the strong absorption of visible light by the electrolyte, and forces illumination of the device through the photoanode with reduction of the global conversion efficiency. A significant driving force (~0.6 V) exists for the regeneration of dye molecules, which constitutes an energy loss: the redox potential of the sensitizer cation and of the I^-/I_3^- mediator are ~1.0 V and ~0.4 V

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vs. NHE, respectively [5]. Finally, due to the use of the I_3^-/I^- mediator, the maximum photovoltage reached in conventional DSSCs is ~0.7–0.8 V.

Another type of solar cell, called electrochemical photovoltaic cell (EPC), consists of an *n*-type (photoanode) and/or a *p*-type (photocathode) semiconducting material in contact with an electrolytic medium, which can be solid (polymer), gel or liquid, containing one redox couple. The electrolytic medium is also in contact with an auxiliary electrode (anode or cathode) which is generally a conductive glass substrate (indium tin oxide, ITO, or fluorine-doped tin oxide, FTO) coated with a catalyst. The operating principle of an EPC primarily involves the illumination of the semiconductor via the transparent auxiliary electrode. If the energy of light radiation $(h\nu)$ is greater or equal to the semiconductor band gap energy (E_g) , electron (e^-) -hole (h^+) pairs are generated. The photogenerated holes (valence band) of an *n*-type semiconductor will migrate to the semiconductor electrolyte interface and oxidize the reduced species of the redox couple present in the vicinity of the electrode (photo-oxidation: $A + h^+ \rightarrow A^+$). After being promoted to the semiconductor conduction band level, the electrons will reach the external circuit via an ohmic contact to the counter electrode where they will reduce the oxidized species that have migrated: $A^+ + e^- \rightarrow A$.

Gerischer and Gobrecht [6] have made the first demonstration of the conversion of light energy into electricity using an EPC; they employed the following configuration: *n*-CdSe1aqueous Fe(CN) $_{6}^{3-/4-}$ ISnO₂. However, it was shown that the low-band gap semiconductor1aqueous electrolytic medium junction generates a phenomenon called photocorrosion (dissolution of the semiconductor, leading to cell instability) [7,8]; the use of an organic solvent was then considered. However, the volatility of such solvents, a particular problem under illumination (increase of the cell temperature), produces an increase of pressure that may lead to mechanical failure of the device. On the other hand, organic solvents can dissolve the adhesive material used to seal the cells.

Another option is to use polymer electrolytes composed of a polymer matrix complexing an alkali metal salt. The nature of these conducting materials has been highlighted by Wright in the seventies [9]. Vijh and Marsan [10] were the first to use a solid polymer electrolyte in contact with a polycrystalline semiconductor; the configuration of the solar cell was *n*-CdSe1 modified PEO_y-M₂S/xS1ITO, where M = Li, Na or K, y = 16, 30 or 60 and x = 1, 3, 5 or 7. Inorganic polysulfides were employed because they may undergo preferential photo-oxidation and thereby protect *n*-CdSe from photocorrosion. Modified PEO represents a co-polymer based on polyethylene oxide, $(CH_2CH_2O)_n$, and the *y* index indicates that the polymer electrolyte has *y* monomer units (CH_2CH_2O) per M₂S molecule.

The weak electrolyte ionic conductivity ($\sim 10^{-6} \, \mathrm{S \, cm^{-1}}$ at 50 °C) and the corresponding low cell energy conversion efficiency have encouraged Philias and Marsan to pursue the research with a new cell configuration, *n*-CdSe|modified PEO₁₂-CsT/0.1T₂|ITO, where T⁻ stands for 5mercapto-1-methyltetrazole ion and T₂ is the corresponding disulfide form [11]. The addition of T₂ (oxidized species) improves the kinetics of the T^{-}/T_{2} redox couple, especially for the reduction process. The choice of a cyclic and unsaturated redox couple, instead of an inorganic polysulfide, was motivated by the stabilization of the reduced species through delocalization of the negative charge. This situation promotes dissociation of the CsT salt in aprotic and polymeric media, and the reduction process leading to a more positive redox potential (potentially enhancing the device photovoltage). Nevertheless, the difficulty of establishing an effective semiconductor polymer electrolyte junction, particularly when the semiconductor is very porous, has prompted researchers to consider alternatives such as gel electrolytes.

These systems, which result from the incorporation of a liquid electrolyte into a polymer matrix, have been described for the first time by Feuillade and Perche [12]. Renard et al. [13] have developed a series of gel electrolytes with the following optimal composition: PVdF (24%) and DMSO/DMF (40/60% v/v) (76%)/1.34 M CsT/0.13 M T₂. 24% represents the mass ratio between the polymer and the polymer-solvent

mixture. PVdF is polyvinylidene fluoride, $(-CH_2-CF_2-)_n$ DMSO is dimethyl sulfoxide and DMF is dimethylformamide. This gel shows an interesting ionic conductivity of 7.1×10^{-3} S cm⁻¹ at 25 °C. However, under extended illumination, drying of the gel was observed. The use of highly conductive and low volatility liquid electrolytes, such as ionic liquids, is of great interest. Indeed, ionic liquids possess a high concentration of ions, they are liquid over a wide temperature range and with a negligible vapor pressure [14,15]. Among them, salts formed by an imidazolium cation and an organic anion are chemically very stable [16,17]. A large number of ionic liquids based on the 1-ethyl-3-methylimidazolium (EMI⁺) cation present a large electrochemical stability window (>4 V) and a high ionic conductivity at 25 °C (>10⁻³ S cm⁻¹). The imidazolium cation coupled with the bis(trifluoromethanesulfonyl)imide (TFSI⁻) counter ion has been used in solar cell devices [18] and Li-ion batteries [19].

The use of aromatic or ring unsaturated derivatives compounds different from CsT and T₂ can be considered in EPCs. As an example, 2mercapto-5-methyl-1,3,4-thiadiazole (McMT) derivatives have been the subject of redox mechanistic studies in aprotic polar solvent (CH₃CN). The work of Shouji and Buttry [20] was done in the field of secondary lithium batteries which have similarities with EPC problematics. Later, Hammami et al. [21] showed that thiolate/disulfide redox couples like 2-mercapto-1,3,4-thiadiazole derivatives, for instance, could be good candidates for application in EPCs or DSSCs. In 2010, Wang et al. [22] presented the first example of a triiodide/iodide-free redox couple based on a thiolate/disulfide redox couple (1-methyl-1H-tetrazole-5-thiol tetramethylammonium salt and its dimer form) for application in a DSSC device. Using this iodide-free redox electrolyte in conjunction with a sensitized heterojunction has allowed reaching an unprecedented efficiency of 6.4% under standard illumination test conditions. Noteworthy, the work of Tian et al. [23], who have employed the 2-mercapto-5-methyl-l,3,4-thiadiazole ion (McMT⁻)/disulfide (BMT) redox couple, demonstrated again the great potential of thiolate/disulfide redox couples in DSSCs.

The EPC developed in our laboratory uses a mixture of aromatic or unsaturated thiolate and disulfide as redox couple. Photo-oxidation of the thiolate species into disulfide takes place at the *n*-type semiconductor electrode while the reverse reaction occurs at the cathode. In order to improve the efficiency of the electroreduction process, which limits the cell performance, Marsan and Bourguignon [24] have developed a catalyst based on a new methodology for cobalt sulfide electrodeposition onto an ITO substrate. Burschka et al. [25] have reported the replacement of platinum by CoS as the counter electrode in DSSCs which showed the great potential of this catalyst for DSSCs working with a thiolate/disulfide redox couple; the electrode stability is still to be improved.

The present work reports the study of the electrolyte based on a thiolate/disulfide redox couple derived from 5-trifluoromethyl-1,3,4-thiadiazole-2(3H)-thione (TfmTT) **1** dissolved in an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMITFSI). In the first part of this study, the synthesis and the chemical characterization of **1**, potassium 5-trifluoromethyl-1,3,4-thiadiazole-2-thiolate (TfmTT⁻ K⁺) **2** and its disulfide form, 5,5'-bis(2-trifluoromethyl-1,3,4-thiadiazole) disulfide (BTfmT) **3**, are presented. A potassium salt has been preferred over a cesium salt because it is less expensive. Fig. 1 shows the structure of the three compounds.

Contrary to Tian et al. [23], 2-mercapto-1,3,4-thiadiazole derivatives (salt and disulfide) presented in this study were substituted with a trifluoromethyl group instead of a methyl group. This functional group may strongly influence the redox processes due to inductive effect on the thiadiazole ring. For instance, Antonello et al. [26] have shown the influence of a series of electron-donating and -withdrawing substituents on the reduction of para-substituted diaryl disulfides derived from 1-mercaptobenzene. One major influence of the electron-withdrawing groups, such as NO₂, CN and F, is on the cathodic peak potential

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