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Stability-enhanced indium hexacyanoferrate electrodes: Morphological characterization, *in situ* EQCM analysis in nonaqueous electrolytes and application to a WO_3 electrochromic device

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ABSTRACT

This paper presents a promising transparent counterelectrode system for a WO_3 electrochromic device (ECD) on the basis of a stability-enhanced indium hexacyanoferrate (InHCF) electrode and a $NaClO_4$/propylene carbonate (PC) electrolyte. Through SEM characterization it was found that clusters of granular InHCF nanoparticles (ca. 80–140 nm) were deposited on ITO substrates in HCl and KCl-stabilized plating solutions, and uniform micrometer thick films with high charge capacity could be obtained. From *in situ* electrochemical quartz crystal microbalance study, it was discovered that Na^+ would enter or move out from the InHCF film in the “desolvated” form during the redox process in a PC electrolyte. Besides, $NaClO_4$/PC resulted in higher electrochemical activity and reversibility than $LiClO_4$/PC. With these discoveries, a durable WO_3-InHCF ECD featuring blue-to-colorless electrochromism was fabricated successfully. The device remained 73.6 and 88.7% of its initial ΔT values at 600 and 800 nm after 40,000 rapid and successive coloring/bleaching cycles, respectively. Moreover, the cycling-induced loss of electrochromic performance almost completely restored after 1-month rest and kept unchanged for another month. Thus, the applicability of this nonaqueous InHCF counterelectrode system to ECDs was verified.

1. Introduction

In response to the continuous energy crisis, several advanced solar technologies to realize low energy-consuming, comfortable buildings and transportation have been proposed and innovated for decades. Among them, electrochromic windows (they are often referred to as “smart windows”) [1] that modulate solar transmission with a low dc bias and allow automatic daylighting control [2] have been proven beneficial for energy-saving applications. Cathodically coloring tungsten oxide (WO_3) is one of the high-efficiency materials for smart window applications and has been proven commercially viable [1,3]. In order to assemble a WO_3 electrochromic device (ECD), a variety of anodically coloring counterelectrodes (also called “ion-storage electrodes”) have been investigated intensively, such as nickel oxide [1,4], Prussian blue (PB) [5], polyaniline (PANI) [6], and so on. Considering an increasing need of developing more and more viable electrochromic systems, we aimed to better exploit a relatively new counterelectrode—indium hexacyanoferrate (InHCF) [7,8] in a WO_3 ECD assembly in this study. Being a PB analogue (metal hexacyanoferrates) [3], InHCF shows high-symmetry and facile redox behavior similar to PB. On the other hand, the optical property of InHCF is quite different from the blue electrochromism of PB and features a trivial colorless-to-pale yellow change upon oxidation [7,8]. Hence it can serve as a transparent ECD counterelectrode like other colorless (or very light color) ion storage layers based on V_2O_5 [9,10], TiO_2 [11,12] and CeO_2 [12,13]. An ECD with a transparent counterelectrode gets rid of redox or optical matching problems between two electrodes and guarantees a transparent state for glazing purposes. In addition, such an ECD can be simply constructed in ambient environment without precoloring electrodes. (Note: When using an anodically coloring counterelectrode like PB, WO_3 is usually reduced to the blue M_xWO_3 state just before ECD assembly in order to pursue better coloration efficiency. This procedure is called precoloring [5]. However, it might introduce the at-rest stability problem for the ECD.)

The present study continues our long-term focus on the electrodeposited InHCF film for ECD applications. In order to acquire a high-quality film with good adhesion and high charge capacity, our efforts had been made to tackle the problem on cyclic voltammetric (CV) deposition [14]. It had been found that the deposition efficiency and stability of a plating solution (an aqueous mixture of 10 mM $InCl_3$ and 10 mM $K_3Fe(CN)_6$) could be greatly improved

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by adding a large amount of KCl and HCl, say 1 M [14]. With the improvement, a series of InHCF-based ECDs had been fabricated, including WO_3-InHCF [15,16], PB-InHCF [17,18] and PANI-InHCF [19] devices. In particular, it had been also found that a WO_3-InHCF device was not only a potential smart window prototype but also a functional thin-film battery ($V^{o}_{Cell} = \text{ca. } 1.24\,V$) visualizing its residual charge [15,16]. These InHCF-based ECDs had been designed to use a polymer electrolyte in order to prevent InHCF from peeling off the conductive glass substrate, as poor cycling stability and quick at-rest decomposition were commonly encountered in aqueous electrolytes [8,20,21]. Hence, a water-based, KCl-doped poly-2-acrylamido-2-methylpropane sulfonic acid (namely, K-PAMPS) had been chosen and provided two sorts of counter ions (K^+ and H^+) for InHCF and electrochromic electrodes in ECDs [15–19]. However, the InHCF-based ECDs with a binder-like K-PAMPS electrolyte only reached a cycle life of 10^3 cycles [16,18]. The stability problem might arise from the insertion of hydrated K^+ ions into InHCF microstructures upon reduction, since this mechanism would gradually cause the film dissolution in water as reported in the literature [20]. Hence, nonaqueous electrolytes would be necessary for developing a promising InHCF counterelectrode system. In addition, microstructural characterization might clarify the preparation of stability-enhanced InHCF electrodes.

In this paper the microstructural morphologies of differently prepared InHCF films will be compared at first. It will be seen that thick, nanoparticulate InHCF films can be formed on the indium tin oxide (ITO) surface from a 1 M HCl and KCl-stabilized plating solution. In addition, it will also be shown that HCl is a more effective plating additive than KCl for growing an InHCF film with high charge capacity. Considering that the stability problem was resulted from aqueous environments, we have also investigated nonaqueous InHCF redox mechanisms in the presence of Na^+ and Li^+ propylene carbonate (PC) electrolytes. The roles of Na^+ and Li^+ in nonaqueous InHCF electrochemistry will be clarified with voltammetric and *in situ* electrochemical quartz crystal microbalance (EQCM) data. Finally, we will demonstrate a highly durable WO_3-InHCF ECD assembled with a $NaClO_4$/PC electrolyte and discuss the electrochromic performances and operating stability of this ECD.

2. Experimental

All chemicals were ACS reagent grade and used as received without further purification, and all aqueous solutions were prepared with deionized water. Indium tin oxide (ITO) glass substrates ($R_{sh} = 7\,\Omega/\square$, dimensions = 4.0 cm × 3.0 cm × 0.07 cm) with a centralized, active area of 2.0 cm × 2.0 cm were used for preparation of both InHCF and WO_3 thin film electrodes. The experimental details of substrate cleaning and InHCF electrodeposition (cyclic voltammetric deposition) were mostly identical to those reported in our earlier paper [16]. Unless otherwise specified, the InHCF films were deposited onto ITO substrates by cycling the potential between 0.1 and 1.2 V (vs. Ag/AgCl/sat'd KCl, at a scan rate of 0.2 V/s) from ten to thirty times, and the plating solution contained 10 mM $InCl_3$, 10 mM $K_3Fe(CN)_6$, 0.1 M KCl and 1 M HCl. For ECD assembly, 30-cycle InHCF films (charge capacity = ca. 15.5 ± 1.5 mC/cm^2, film thickness = ca. 1.5 μm) were used. Scanning electron microscope (SEM) pictures of fresh (as-grown) InHCF films were taken using the Hitachi S-800 Field Emission Scanning Electron Microscope. The redox properties of InHCF/ITO electrodes in 1 M $LiClO_4$/PC and 1 M $NaClO_4$/PC were characterized by three-electrode cyclic voltammetry (CV) with an Ag/AgCl/sat'd KCl reference electrode and a platinum auxiliary electrode. In addition, *in situ* electrochemical quartz crystal microbalance (EQCM) analysis was done to study the counter ion insertion/extraction for the redox reaction of InHCF in the PC electrolytes. For EQCM experiments, 20-cycle InHCF films were grown onto gold-coated QCM chips (CH Instruments; active area = 0.196 cm^2; fundamental frequency = 7.995 MHz) by the CV deposition with a reduced potential window (0.1–0.85 V at 0.2 V/s). The *in situ* resonant frequency change during the redox process was monitored with a programmable EQCM (EG&G, model QCA-917). After experiments, frequency data were converted to mass change data according to vendor's protocols and the Sauerbrey equation [22].

Tungsten oxide films were prepared by a sol–gel method coupled with spin coating. The peroxoacetatotungstic acid precursor (an alcohol sol) was prepared according to literature [23]. To attain a deep blue color state, each WO_3 electrode was prepared by repeated spin coating of multiple sol–gel layers on one ITO substrate. For deposition of each layer, the alcohol sol was spin coated on the substrate at 600 rpm for 3 s and then at 2000 rpm for another 15 s. A 10 min soft bake at 100 °C was carried out when every two layers of sols were coated. After eight spin coatings, a final 1 h hard bake at 200 °C was done to form a WO_3/ITO electrode. The ECD was assembled with fresh, nonpolarized WO_3 and InHCF electrodes in air and at room temperature. By applying 2 mm thick spongy-rubber spacers to the inner edges of an ECD, a mini-chamber between the WO_3 and InHCF electrodes was formed and was then filled with 1 M $NaClO_4$/PC electrolyte. Afterward, the ECD was clipped tightly and sealed with epoxy resin before testing. The sandwiched ECD configuration can be described as ITO/WO_3/1 M $NaClO_4$, PC/InHCF/ITO. *In situ* equilibrium and transient spectroelectrochemical measurements were performed to characterize the electrochromic performances and operating stability of an ECD. The transmittance spectra were collected by a programmable UV/visible spectrophotometer (Jasco, V-530). All electrochemical measurements were carried out with a programmable potentiostat/galvanostat (Autolab, PGSTAT30) and at room temperature (25 °C).

3. Results and discussion

3.1. SEM characterization of electrodeposited InHCF films

3.1.1. Influences of KCl and HCl additives on the CV deposition

Cyclic voltammetric (CV) deposition (potential-cycling electroplating) using an aqueous mixture of In^{3+} and $Fe(CN)_6{}^{3-}$ is a typical approach to grow an InHCF film. In particular, a diluted (few mM) aqueous mixture frequently served as the deposition bath to prepare a very thin InHCF film (several μC/cm^2) for electrocatalytic [24] and sensor [25] applications. By contrast, a film with several mC/cm^2 charge capacity (surface charge density) is required for ECD's counterelectrode purpose [9–13]. However, preparation of a thick and uniform film had been problematic, since the chemical reduction of $Fe(CN)_6{}^{3-}$ into $Fe(CN)_6{}^{4-}$ would take place and then co-precipitate with In^{3+} instantaneously to yield colloidal $In_4[Fe(CN)_6]_3$ agglomerates ($K_{sp} = 2 \times 10^{-44}$ [26]) in a concentrated plating solution (say, 10 mM In^{3+}–ferricyanide mixture). Our efforts had been made to tackle this problem, and it had been proven electrochemically that both the stability of a plating solution and the deposition efficiency could be greatly improved by adding a large amount of KCl and HCl [14]. To further evidence the effect of enhanced deposition by KCl and HCl additives, we carried out microstructural comparison between the InHCF films grown on ITO electrodes in the presence of 1 M KCl, 1 M HCl, or both in this work and the results are presented in Fig. 1.

Fig. 1 gives the SEM images of three 20-cycle InHCF films prepared from different plating solutions: (a) 10 mM $InCl_3$, 10 mM $K_3Fe(CN)_6$ and 1 M KCl; (b) 10 mM $InCl_3$, 10 mM $K_3Fe(CN)_6$ and 1 M HCl; (c) 10 mM $InCl_3$, 10 mM $K_3Fe(CN)_6$, 1 M KCl and 1 M HCl. It can