Degradation Analysis of Electrochromic Devices

Using a New Method

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ABSTRACT

In this work, polyFe and NiHCF thin films for the electrochromic devices were fabricated by a spray coating method which was used as working and counter electrodes, respectively. Based on a long-term cycling test, we investigated the performance degradation phenomenon of the polyFe-based electrochromic devices (ECD) using photos and movies.

1 Introduction

A material's ability to change color in response to an electrical stimulation, such as the introduction of a weak electric field, is known as electrochromism. This happens as a result of optical variations in absorbance, transmittance, or reflectance. These optical transitions are caused by an electrochemically triggered oxidation-reduction reaction, leading to the material switching from a transparent (bleached) state to a colored one, or from one colored state to another. An electrochromic device (ECD) is made up of three layers, the electrochromic active layer, the electrolyte, and the ion storage layer. For real-world uses of ECDs, great visual contrast, quick color change, low voltage of operation, and excellent long-term use are required. EC display devices such as smart windows2 have drawn a lot of interest in reducing the energy consumption of air conditioning in workplaces or vehicles. Low voltage for EC switching is predicted to improve ECD longevity for repeated coloring by reducing electric damage to the EC materials. Despite continuous progress in related fields, it has long been difficult to figure out how to make electrochromic meet mature displays' requirements (such as excellent overall performance). As a result, the commercialization of relevant high-quality products is still in its early stages. The performance of traditional EC materials and devices still has difficulty meeting the practical requirements of displays.

Until now very few studies have reported on the EC device durability and degradation mechanism, which plays a crucial role in EC device commercial applications. Some possible causes of ECD degradation are the resistance of the ITO electrodes, the influence of the polymer chain, the interface between polymer and counter anion, low conductivity of the electrolyte, the resistivity of the counter materials, and overpotential at elevated temperatures.

Therefore, our aim is to investigate the performance degradation phenomenon & study the mechanism of ECD using image data analysis. Evaluating the factors that cause the degradation of the device and studying the appropriate solutions for degradation.

2 Experiment

2.1 Synthesis of Metallo-Supramolecular Polymer (polyFe)

The polyFe supramolecular polymer was synthesized by the 1:1 complexation method of the ligand (L1) [4',4'''-(1,4-Phenylene) bis (2,2'6',2'''-terpyridine) with iron (II) acetate [C6H5FeO4] salt, according to the previously reported paper2. The ligand (L1) is mainly a terpyridine-based ditopic ligand which has been prepared using the procedure described in the paper4.

2.2 Preparation of polyFe thin film

The polyFe thin film on the indium tin oxide (ITO) glass substrate was prepared by spray-coating method from a methanol solution of Fe polymer (3 mg/ml).

2.3 Fabrication of solid-state device (ECD)

Solid-state electrochromic devices (ECDs) composed of Fe(II) based metallo-supramolecular polymer (polyFe) (an electrochromic layer) and Nickel hexacyanoferrate (NiHCF) (an ion storage layer) thin films were fabricated by a spray coating method on the ITO substrates which were used as working (WE) and counter (CE) electrodes, respectively (Fig. 1a). The transparent gel electrolyte thin film was prepared by mixing PMMA, propylene carbonate (PC), and LiClO4 salt in an 8/46/46 (w/w) ratio. The WE and CE were placed in a sandwich configuration separated by the transparent gel film, followed by annealing at 95 °C and 40% relative humidity.

3 Results and Discussions

The average thickness of polyFe film on the ITO substrate was ~ 150 nm. The purple color methanol solution of Fe polymer showed an absorption maximum at ~580 nm for metal-to-ligand charge transfer transition.
(MLCT) in the UV-visible spectrum. The ECD displayed bleaching and coloring at a very low potential at 1.0 V.

Besides, from the chronoamperometric test, we investigated the performance degradation phenomenon of the ECD by taking photos and movies. During the chronoamperometric test, we took images of ECD at each cycle to understand the electrochromic color changes in the device. For the first cycle, these images showed that the device changed its color from purple to colorless in less than 2 seconds. After the 500th cycle, the device was not able to show a completely bleached state within the same time framework.

For the image data analysis of ECD, we took movies of the device during the cyclic test to record the color changes for each cycle. From movies, images were extracted from where we extracted the pixel values using Python software. Using the pixel values time vs. contrast graph was plotted (Fig. 1b). The graph showed a sharp change of color to a colorless state for the 1st cycle, in the case of the 500th cycle the change was not sharp. This analysis indicates that during the cyclic test, the performance of the response time of the device becomes slower with the increase of cycle number.

4 Conclusions
During cyclic testing, some degradations are identified for electrochromic devices. Many of these mechanisms are specific to the materials, device design, and operating conditions used. The electrochromic properties of the polyFe thin film degraded significantly as the cycle number increased. This new method for degradation analysis has some advantages including the low production cost and commercial applications. Low working voltage is highly desired in terms of ECD longevity. This new method is expected to open a new path for the degradation analysis of ECDs for commercial applications.

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