



In operando XAFS experiments on flexible electrochromic devices based on Fe(II)-metallo-supramolecular polyelectrolytes and vanadium oxide



Marco Schott^{a,b}, Wojciech Szczerba^{c,e}, Uwe Posset^a, Angela Šurca Vuk^d, Matthias Beck^b, Heinrich Riesemeier^c, Andreas F. Thünemann^c, Dirk G. Kurth^{b,*}

^a Fraunhofer-Institut für Silicatforschung ISC, Neunerplatz 2, D-97082 Würzburg, Germany

^b Julius-Maximilians-Universität Würzburg, Chemische Technologie der Materialsynthese, Röntgenring 11, D-97070 Würzburg, Germany

^c BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, D-12205 Berlin, Germany

^d National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

^e AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology (ACMiN), Al. Mickiewicza 30, 30-059 Krakow, Poland

ARTICLE INFO

Article history:

Received 10 April 2015

Received in revised form

29 September 2015

Accepted 14 October 2015

Keywords:

Metallo-supramolecular polyelectrolytes

Vanadium oxide

Electrochromism

Electrochromic device

Cyclic voltammetry

XAFS

ABSTRACT

Flexible electrochromic devices (ECDs) based on Fe(II)-metallo-supramolecular polyelectrolytes (Fe-MEPE) and vanadium oxide are studied *in operando* by means of x-ray absorption fine structure (XAFS) spectroscopy. The ECDs are blue–purple in the colored state at 0.0 V and become light yellow when a voltage of 1.6 V is applied. The XAFS studies at the K-edge of Fe(II) reveals that the absorption edge is shifted toward higher energies by 1.8 eV in the transparent state. Comparison of two different ECDs and different charge cycles demonstrates the reversibility and repeatability of the process. We attribute the shift to a charge transfer and a change of oxidation state of the ions from Fe²⁺ to Fe³⁺. The transition is not accompanied by a noticeable structural change of the octahedral coordination geometry as confirmed by analysis of the extended x-ray absorption fine structure (EXAFS) data.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Electrochromic (EC) materials are able to change their optical properties due to redox reactions induced by application of a low electrical voltage [1,2] and thus, they are attractive for applications such as smart windows or electronic paper [3]. Using EC technology, it is possible to reduce energy consumption (e.g. via reduced air conditioning needs) and increase indoor comfort in buildings and vehicles. However, important drawbacks of commercial electrochromic products can be seen in their high price and slow response, in particular for large-area devices such as architectural glazing. A new type of cathodically coloring EC materials are metallo-supramolecular polyelectrolytes (MEPE), which have thoroughly been investigated in recent years [4–7]. Responsible for the coloration of these metallo-polymers is a strong metal-to-ligand charge-transfer (MLCT) transition, causing strong optical absorption in the visible range. Fe-MEPE consisting of Fe(II) ions, bis(terpyridine) ligands and acetate (OAc[−]) counter

ions shows outstanding electrochromic properties and exhibits a reversible color change upon oxidation from Fe²⁺ (blue) to Fe³⁺ (colorless) and vice versa. MEPEs show high contrast ratios, short response times, high cycle stability and high coloration efficiencies [8]. By employing wet-chemical processing, e.g. layer-by-layer deposition [9] or dip-coating [10], for fabricating MEPE thin films, a high potential for cost reduction is anticipated in comparison to inorganic electrochromic materials such as tungsten oxide (WO₃) [11,12] or nickel oxide (NiO_x) [13,14] prepared by expensive vacuum techniques. Metallo-polymers are synthesized by metal ion coordination of suitable metal ions, such as Fe, Co, Cu, Ru, Ni, Zn and a ditopic ligand such as 1,4-bis(2,2':6',2''-terpyridine-4'-yl)benzene [15,16].

We report for the first time an *in operando* investigation of a MEPE based ECD by x-ray absorption fine structure (XAFS) spectroscopy [17]. In the XAFS technique, x-ray photons excite core electrons of a given chemical element. The excited photoelectron probes the unoccupied energy levels of the absorbing atom giving information, among others, on oxidation state and coordination structure. This part of the spectrum is referred to as x-ray absorption near-edge structure (XANES). XANES is sensitive to a change in oxidation state, which is usually observed by a shift of

* Corresponding author. Tel.: +49 931 31 82631; fax: +49 931 31 82109.

E-mail address: dirk.kurth@matsyn.uni-wuerzburg.de (D.G. Kurth).

the absorption edge on the energy scale. If the excitation energy is sufficiently high for the photoelectron to leave the absorbing atom, the quasi-free photoelectron is being scattered off the neighboring atoms. These scattering events cause an interference modifying the absorption spectrum in form of oscillations known as the extended x-ray absorption fine structure (EXAFS). A Fourier transform analysis of the EXAFS oscillations provides information on the local geometry around the absorbing atom. Thus, XAFS spectroscopy is a valuable tool for probing the local chemistry and structure of a selected element.

In this study, a novel flexible electrochromic device (ECD) configuration based on Fe-MEPE and vanadium oxide (V-oxide) thin films fabricated by dip-coating on transparent conducting electrodes is explored. V-oxide proved particularly useful as a counter electrode material for Fe-MEPE due to its good ion storage capability and the fact that it does not disturb the XANES and EXAFS measurements at the *K*-edge of iron at 7112 eV.

2. Experimental

2.1. Fe-MEPE electrode

Following a previous study, Fe-MEPE thin films on ITO (indium tin oxide)-coated poly(ethylene terephthalate) (PET) films were fabricated using a dip-coating method at room temperature and subsequent annealing step at 60 °C for 24 h [8]. To the coating solution a proprietary polyurethane–polysiloxane binder prepared by sol–gel processing was added to ensure good adhesion and film forming properties. The PET-ITO film employed had a thickness of 127 μm and a sheet resistance of 50–60 Ω/sq (OC50, Solutia Inc.).

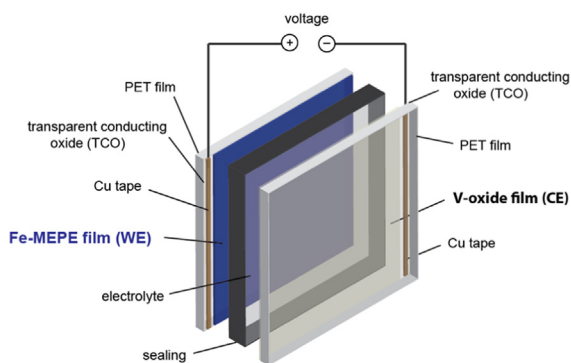


Fig. 1. Assembly of an electrochromic device (ECD) with a Fe-MEPE film on PET-ITO as the working electrode (WE), a V-oxide film on PET-ITO as the counter electrode (CE) and an electrolyte layer in between.

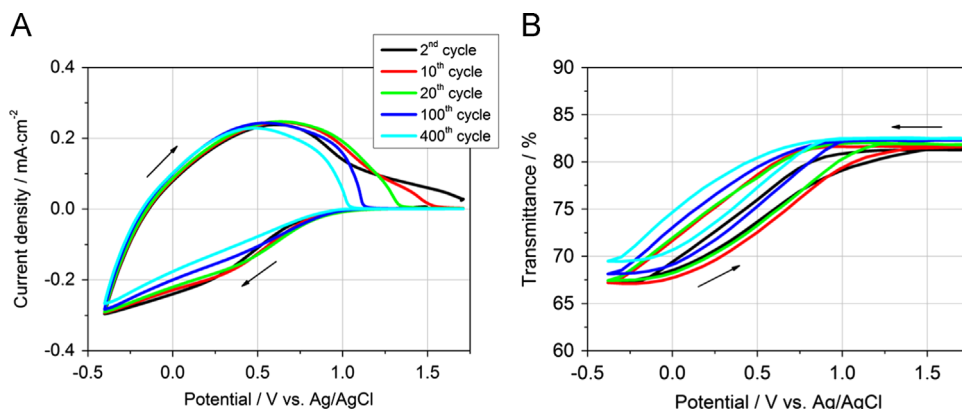


Fig. 2. UV-vis spectro-electrochemical measurements of a V-oxide thin film deposited on PET-ITO during cyclic voltammetric cycling up to 400 cycles from 1.7 V to –0.4 V vs. Ag/AgCl. The transmittance change is recorded at 634 nm.

2.2. Vanadium oxide electrode

The V-oxide films were prepared from a 1 M solution of vanadium(V) oxoisopropoxide in isopropanol identical to the one used for low-temperature deposition of films via spin-coating in an earlier work [18]. For this study, the films were deposited by dip-coating on ITO-coated PET film of dimensions 5 × 5 cm². The withdrawal speed was 100 mm min^{–1}. The as-deposited films were treated thermally at 150 °C for 30 min. The V-oxide sols remain stable at temperatures below 4 °C for some months.

X-ray photoelectron spectroscopy (XPS) analysis was carried out by means of a surface Science Instruments (California) S-Probe instrument equipped with a monochromatic Al K_α excitation source. The electron spectrometer was a concentric hemispherical analyzer with constant pass energy of 150 eV and an electron acceptance angle of 30°. The binding energy values were charge corrected to C 1s at 285.0 eV and peak fitting was done after subtraction of a standard Shirley background.

In situ spectro-electrochemical measurements of the V-oxide electrodes were performed in a three-electrode glass cell with quartz windows for passing light in the spectral range from 300 nm to 1100 nm. The cell was placed in a sample compartment of a diode array HP8453 spectrophotometer, filled with 40 ml of 1 M LiClO₄/PC electrolyte. The spectra were recorded referencing against a cell filled with electrolyte only. The V-oxide film (working electrode) was positioned in the center of the optical beam path, while the counter (Pt rod) and reference (Ag/AgCl) electrodes were carefully placed outside of the optical beam path. The cyclic voltammetric measurements were performed in the potential range from 1.7 V to –0.4 V and at a scan rate of 20 m s^{–1} using a PGSTAT 302 N potentiostat.

2.3. Electrochemical characterization of the ECDs

The electrochemical measurements were performed with a Solartron Multistat 1470E potentiostat. The UV-vis spectra were measured with an Avantes AvaSpec-2048 standard fiber optic spectrometer combined with a balanced deuterium–halogen light source. All measurements were done at room temperature. The electrochemical and *in situ* spectro-electrochemical characterization was performed using an electrochromic device with Fe-MEPE and V-oxide as working and counter electrode materials, respectively, and 1 M LiClO₄/PC thickened with a thermoplastic polymer as a gel electrolyte. The visible light transmittance, τ_v , was calculated according to DIN EN410:

$$\tau_v = \frac{\sum_{380\text{nm}}^{780\text{nm}} D_\lambda \cdot \tau(\lambda) \cdot V(\lambda) \cdot \Delta\lambda}{\sum_{380\text{nm}}^{780\text{nm}} D_\lambda \cdot V(\lambda) \cdot \Delta\lambda}$$

Download English Version:

<https://daneshyari.com/en/article/6534809>

Download Persian Version:

<https://daneshyari.com/article/6534809>

[Daneshyari.com](https://daneshyari.com)