Solar Energy Materials & Solar Cells ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Electrochromic performance of nanocomposite nickel oxide counter electrodes containing lithium and zirconium

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ARTICLE INFO

Keywords:
Nickel oxide
Nanocomposite
Oxidation state
Electrochromic
Li stoichiometry

ABSTRACT

Nickel oxide materials are suitable for counter electrodes in complementary electrochromic devices. The state-of-the-art nickel oxide counter electrode materials are typically prepared with multiple additives to enhance peformance. Herein, nanocomposite nickel oxide counter electrodes were fabricated *via* RF magnetron co-sputtering from Ni–Zr alloy and Li_2O ceramic targets. The as-deposited nanocomposite counter electrodes were characterized with inductively coupled plasma mass spectrometry (ICP-MS), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS). It was found that the stoichiometry, crystal structure and electronic structure of the nickel oxide-based materials could be readily tuned by varying the Li_2O sputter deposition power level. Comprehensive electrochromic evaluation demonstrated that the performance of the nickel oxide-based materials was dependent on the overall Li stoichiometry. Overall, the nanocomposite nickel oxide counter electrode containing lithium and zirconium synthesized with a Li_2O deposition power of 45 W exhibited the optimal performance with an optical modulation of 71% and coloration efficiency of 30 cm^2/C at 670 nm in Li-ion electrolyte.

1. Introduction

Electrochromic effects in transition metal oxide materials (*e.g.*, nickel oxide, tungsten oxide, titanium oxide) have received extensive attention for smart windows, rear-view mirrors and non-emissive displays. A cathode/anode complementary electrode configuration in electrochromic devices is the most prevalent configuration due to the advantages this configuration offers, *i.e.*, color neutrality and coloration efficiency [1,2]. Tungsten oxide and nickel oxide are the most investigated electrochromic cathodic and anodic materials, respectively [2,3]. The successful operation of a complementary electrochromic device requires compatibility between the cathodic and anodic electrodes. The critical electrode compatibility requirements include a balanced charge capacity [4–6] and equivalent switching kinetics [7]. Since the 1970s, extensive efforts have been devoted to improve the performance and mechanistic understanding of the electrochromic process in cathodic tungsten oxide materials [8–11]. Further research has been directed towards developing cost effective syntheses and manufacturing processes for these cathodic materials [2,12]. Conversely, many challenges remain unresolved for anodic nickel oxide counter electrodes, including slow switching kinetics, inferior optical modulation, and poor bleached-state transparency [13–16].

In recent years, significant efforts have been dedicated to optimize the performance of nickel oxide counter electrode materials, with the emphasis on controlling morphology on the nanoscale (nanocomposites) [1,7,17], crystal structure (lattice order, crystallinity) [17,18] and electronic structure [19]. The most promising nickel oxide counter electrodes are composed of complex mixtures of transition metal oxides including secondary additives such as lithium oxide and lithium peroxide [20]. Recently, multicomponent nickel oxide counter electrodes (*i.e.*, nickel oxide materials that contain at least two additives) have shown superior performance relative to the traditional nanocomposite nickel oxide electrodes that contain only one additive [1,20]. The addition of co-additives (*i.e.*, a transition metal and

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http://dx.doi.org/10.1016/j.solmat.2013.11.023

Please cite this article as: F. Lin, et al., Electrochromic performance of nanocomposite nickel oxide counter electrodes containing lithium and zirconium, Solar Energy Materials and Solar Cells (2014), http://dx.doi.org/10.1016/j.solmat.2013.11.023

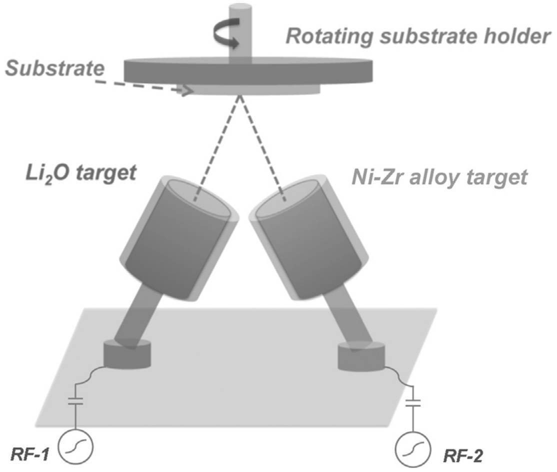
lithium) to the nickel oxide electrode material enables simultaneous improvement of bleached-state transparency, switching kinetics, and optical modulation [1,19,20]. In addition, the nickel oxidation state and hole concentration in nickel oxide-based electrochromic materials are critical for favorable electrochromic performance and relevant specifically to the coloration/bleaching mechanism [19,20]. In our previous study, we demonstrated that lithium is an effective additive for tuning the nickel oxidation state and hole concentration in nickel oxide materials containing aluminum [19]. However, the electrochromic performance (*e.g.*, optical modulation and bleached-state transparency) of these Al-containing nickel oxide nanocomposites was modest compared to the performance reported for nickel oxide materials containing lithium and tungsten [1] or lithium and zirconium [20] additives. The nickel oxide nanocomposite materials containing lithium and zirconium exhibited extremely high electrochromic performance relative to previous electrochromic transition metal oxide materials [20]. However, it is unclear whether or not the hole concentration in these high performing nickel oxide materials containing lithium and zirconium can be optimized further to improve electrochromic performance.

Herein, we extend our previous studies by systematically tuning the Li stoichiometry in radio frequency (RF) magnetron co-sputtering deposition of nanocomposite nickel oxide materials. It is found that the sputtering conditions (*i.e.*, deposition power levels) provide an efficient route for tuning the Li stoichiometry, crystal structure, and electronic structure in nanocomposite nickel oxide materials. The chemical, structural, and electronic properties of these nickel oxide-based materials are characterized in detail and an optimal lithium concentration is determined.

2. Experimental methods

2.1. Electrode preparation

RF magnetron co-sputtering was preformed on an Angstrom EvoVac deposition system housed in a glove box under an argon atmosphere following a previously described method (see Scheme 1) [19]. Three-inch diameter metal alloy target, Ni–Zr (80–20 at%), was purchased from ACI Alloys, while a three-inch diameter Li_2O ceramic target (99.9%) supported on a molybdenum backing plate was purchased from Plasmaterials, Inc. The deposition power level for the metal alloy target was fixed at 60 W, while the deposition power level for the Li_2O ceramic target was adjusted to 0 W, 15 W, 30 W, 45 W and 60 W to control the Li stoichiometry. The resulting nickel oxide-based samples are denoted as Li_2O/0 W, Li_2O/15 W, Li_2O/30 W, Li_2O/45 W and Li_2O/60 W according to the Li_2O deposition power level. The target–substrate distance was 10 cm and remained constant throughout the study, and no additional heating was applied to the substrate. The substrate holder was rotated during the sputtering process. The base pressure and total deposition pressure were 10^{-7} Torr and 2 mTorr, respectively. The Ar/O_2 gas mixture was fixed at 1/2 throughout the study. The fluorine-doped tin oxide (FTO) glass substrates were purchased from Hartford Glass CO, Inc. (TEC 15, 1.5 in. × 0.82 in. × 2.3 mm). The substrates were cleaned successively with soapy water, deionized water, acetone, isopropanol, and dried under flowing N_2. ICP-MS and XRD samples were deposited on aluminum foil and microscope glass, respectively.



Scheme 1. Schematic representation of RF magnetron co-sputtering chamber, where the relative Li_2O deposition power level was adjusted to control the Li stoichiometry in the nickel oxide-based materials.

2.2. Materials characterization

The crystal structures of the resulting films were characterized on a Philips X-ray diffractometer Model PW1729 operated at 45 kV and 40 mA using CuK_α radiation. The samples were prepared for transmission electron microscopy (TEM) using a Nano-Lab 200 Dual Beam FIB and analyzed on a FEI G^2-T30 TEM operating at 300 kV. The ICP-MS used is a Perkin Elmer NexION 300q with an S10 autosampler. Calibration standards for Li, Ni, and Zr were made using SPEX Certiprep ICP-MS standard solutions in 2% HCl (Optima trace metal grade). Dilutions of thin film digest solutions were made in 2% HCl. All dilutions were made in 15 mL Falcon polypropylene centrifuge tubes and analyzed immediately. SEM was done on a JEOL JSM-7000F Field Emission Scanning Electron Microscope with an EDAX Genesis EDS. Soft X-ray absorption spectroscopy (XAS) measurements were performed on the 31-pole wiggler beam line 10-1 at Stanford Synchrotron Radiation Lightsource (SSRL) using a ring current of 350 mA and a 1000 l mm^{-1} spherical grating monochromator with 20 μm entrance and exit slits, providing $\sim 10^{11}$ ph s^{-1} at 0.2 eV resolution in a 1 mm^2 beam spot. During the measurements, all samples were attached to an aluminum sample holder and the surface was connected to the isolated holder using conductive carbon. Data were acquired in a single load at room temperature and under ultra-high vacuum (10^{-9} Torr). Detection was performed in total electron yield (TEY) and fluorescence yield (FY) modes. For TEY, we collected the sample drain current, and a silicon diode (IRD AXUV-100) was used to collect the FY positioned near the sample surface. Contributions from visible light were carefully minimized before the acquisition, and all spectra were normalized by the current from freshly evaporated gold on a fine grid positioned upstream of the main chamber.

2.3. Electrochromic performance evaluation

Electrochromic properties were measured in a liquid electrolyte half-cell where the electrolyte (Novolyte Technologies, part of the BASF Group) was 1 M lithium perchlorate ($LiClO_4$) dissolved in propylene carbonate (PC). Cyclic voltammetry (CV) was carried out using a BioLogic VMP3 multichannel potentiostat with a scan rate of 20 mV/s and a voltage range of 1.7–4.2 V vs. Li/Li^+, and the initial voltage was set at the open circuit voltage. *In situ* transmittance was measured using a diode laser at 670 nm. Switching kinetics (*i.e.*, coloration and bleaching) was measured under potential step cycling from 1.7 to 4.2 V vs. Li/Li^+, where each potential step was maintained for 2 min. The switching speed is defined as the time required to achieve ∼90% of total transmittance change within a potential step. Both switching kinetics and CV measurements were performed for 200 cycles. All electrochemical measurements were carried out under an argon atmosphere

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