Solar Energy Materials & Solar Cells 92 (2008) 914–918

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Application of 1/*f* current noise for quality and age monitoring of electrochromic devices

J. Smulko [a,*], A. Azens [b], R. Marsal [b], L.B. Kish [c], S. Green [d], C.G. Granqvist [d]

[a] Faculty of Electronics, Telecommunications and Informatics, Gdańsk University of Technology, ul. G. Narutowicza 11/12, 80-952 Gdańsk, Poland
[b] ChromoGenics Sweden AB, Märstagatan 4, SE-75323 Uppsala, Sweden
[c] Department of Electrical and Computer Engineering, Texas A&M University, College Station, TX 77843-3128, USA
[d] The Ångström Laboratory, Department of Engineering Sciences, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden

ARTICLE INFO

Article history:
Received 22 July 2007
Received in revised form
21 February 2008
Accepted 22 February 2008
Available online 14 April 2008

Keywords:
Electrochromics
Smart window
1/*f* noise
Tungsten oxide
Nickel oxide
Durability

ABSTRACT

This is a continuation of an earlier study on 1/*f* noise in electrochromic (EC) devices undergoing discharge via a resistor. The EC devices comprised films of W oxide and Ni–V oxide joined by a polymer electrolyte, and with this three-layer stack positioned between transparent conducting In_2O_3:Sn films backed by polyester foils. We also investigated "symmetrical" devices with two identical films of W oxide or Ni–V oxide. The power spectral density S_i at fixed frequency scaled with current (I) as $S_i{\sim}I^2$. Color/bleach cycling for about 2500 times degraded the optical properties and homogeneity of the EC devices and increased the 1/*f* noise intensity by a factor of four, which confirms the earlier assumption that 1/*f* noise has a good potential to serve as quality and aging assessment for EC devices. Studies of "symmetrical" devices proved that the noise was mainly associated with the Ni oxide, and measurements on individual parts of an EC device indicated that the 1/*f* noise originated from localized areas.

1. Introduction

Electrochromic (EC) devices are characterized by their ability to display reversible and persistent changes of their optical properties upon charge insertion/extraction [1]. Such devices have only a few applications in today's technology, but the situation is likely to change so that ECs gets wider uses [2,3]. Among the forthcoming applications one notes architectural "smart windows" capable of achieving energy efficiency together with occupant comfort in buildings and transport vehicles [1–5]. Other applications concern variable-transmittance visors and goggles [6], variable-reflectance mirrors, and non-emissive displays. Long-term durability is an issue of obvious concern with regard to EC devices. A number of studies have concerned durability [7,8], but the need for reasonably fast techniques for quality assessments has remained. This paper explores electronic noise as a possible technique for giving information related to the durability and degradation of EC devices. A brief report on this subject was given before [9].

Electronic noise is a general feature that is well known in conductors, semiconductors, electrolytes, and at electrolyte–electrolyte interfaces [10]. Fluctuations in current (I) and voltage can originate from thermal equilibrium processes or be due to non-equilibrium phenomena. They can give rise to a variety of noise types, known as thermal noise, shot noise, burst noise, generation-recombination noise, 1/*f* noise, and $1/f^2$ noise (where f denotes frequency) [11]. The present investigation considers 1/*f* noise during discharge of EC devices, and with changes of this noise following upon device degradation. 1/*f* noise has been used in the past for monitoring the reliability of electronic [11–15] and ionic [16] devices such as batteries [17], sensors, and transducers [18]. In particular, 1/*f* noise can provide information on corrosion processes [19–22].

2. Device manufacturing and operation

Fig. 1 illustrates an EC device of the type used in this study. Its preparation has been described elsewhere [5,23], and only the most essential features are reported here. A foil of 175-μm-thick polyethylene terephthalate (PET), up to ~50 cm^2 in size, was first coated with transparent and electrically conducting In_2O_3:Sn (i.e., ITO). A 300-nm-thick film of nanoporous W oxide was then applied by reactive DC magnetron sputtering in the presence of some H_2. Another ITO-coated PET sample was coated with a 200-nm-thick film of nanoporous $Ni_{0.93}V_{0.07}$ oxide by DC magnetron sputtering. After treating the Ni-oxide-based film in

* Corresponding author. Tel.: +48 58 3486095; fax: +48 58 3416132.
E-mail address: jsmulko@eti.pg.gda.pl (J. Smulko).

0927-0248/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2008.02.035

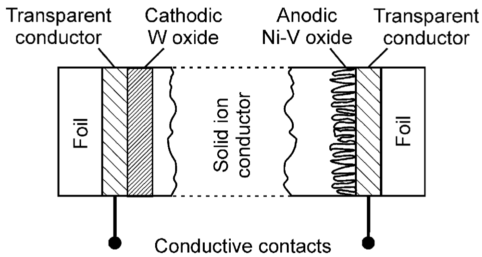

Fig. 1. Structure of an electrochromic device with a central solid ion conductor surrounded by a cathodically coloring W oxide film and an anodically coloring Ni–V oxide film. This three-layer stack is positioned between transparent conductors backed by PET foil.

ozone in order to discharge it [24], the two nanoporous oxide films were joined via a transparent, adhesive polymer electrolyte to form a laminated EC device of the conventional five-layer "battery-type" design. The addition of V makes the Ni target non-magnetic and hence suitable for magnetron sputtering. Otherwise the influence of the V is minor; it produces a weak yellowish tint to the EC device but does not influence the electrochemistry of the device operation [25,26]. The yellowish appearance in the fully discharged state may be desired and lead to an enhanced optical contrast for see-through applications [6]. A more transparent state can be accomplished by replacing the V addition with Al or Mg, i.e., with metals capable of forming wide band gap oxides [5,27]; the latter materials lead to EC devices that are suited for architectural applications.

The laminated EC device appeared slightly grayish-yellowish in its bleached state, as shown in Fig. 2(a). It shifted towards a dark grayish appearance after transferring charge from the Ni-oxide-based film, via the electrolyte, to the W oxide film. The EC sample was colored/bleached by applying a voltage of +1.5/−1.5 V to the ITO films every eighth minute during an approximately 2 week long period. This cycling was chosen to induce degradation and was much harsher than the one normally used for operating EC devices [5,27]. Fig. 2(b) shows the sample in its bleached state after the cycling; it is evident that the treatment has yielded irreversible changes and an appearance of dark areas. After extended aging, some of the EC devices developed persistent spots, as illustrated in Fig. 2(c).

In order to distinguish between effects on the electronic noise from the W oxide and the Ni–V oxide, we also made "symmetrical" devices with either two identical W-oxide-based films or two identical Ni-oxide-based films. Fig. 3(a and b) illustrates the bluish and brownish appearances of devices based on W oxide and Ni oxide, respectively. The application of +1.5/−1.5 V between the ITO films shuttles charge but does not alter the optical properties. We note that "symmetrical" devices, incorporating two films of W oxide or Ir oxide films, have been studied before with the object of shedding light on degradation modes [28].

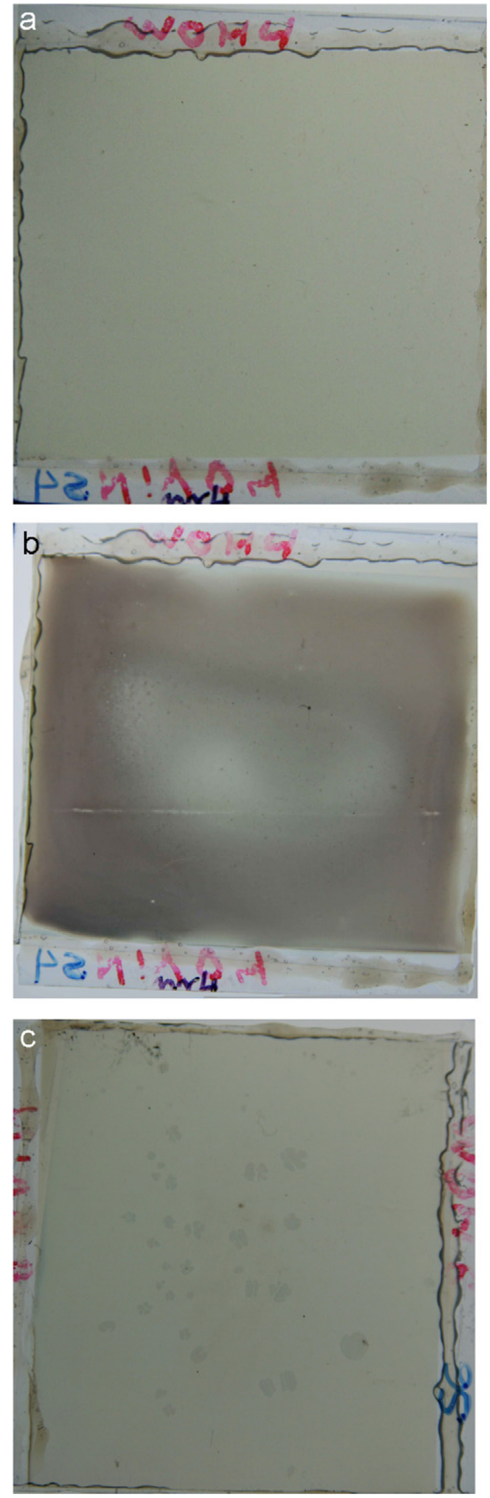

Fig. 2. Electrochromic device, $5 \times 5\,cm^2$ in size, before (a) and after (b) color/bleach cycling as described in the main text; the cycling process led to the appearance of spots in some devices (c).

3. Current noise measurement

Current noise was measured as shown in Fig. 4. The device was discharged via a 1 kΩ resistor R, and current was recorded on a battery-operated low-noise pre-amplifier. The inherent noise of the pre-amplifier was negligible when compared with the voltage fluctuations measured across the resistor. The resistor value is orders of magnitudes less than the differential resistance of the device, and thus the measured normalized voltage fluctuations are equal to the normalized current fluctuations of the device. Electromagnetic and optical shielding was accomplished by putting the device and resistor in a tight metal encasement. Data were recorded at room temperature during the final part of discharging of the device, with $I < 300\,\mu A$ The discharging took up to 30 min. A 30 Hz high-pass filter in the pre-amplifier reduced the low-frequency components.

Fluctuations were sampled at a frequency $f_s = 15\,kHz$ within an interval of less than 5 s in order to register 2^{16} samples each time. The DC current changed less than 2% within this interval,