



Optimized properties of innovative Si–In–Zn–O/Ag/ Si–In–Zn–O electrode for NiO based energy efficient electrochromic heat shutters

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ABSTRACT

Electrochromic heat shutters present an attractive choice for efficient thermal management, designed to decrease energy usage and improve indoor comfort through their capacity to control sunlight. In order to enhance sunlight modulation in the visible spectrum and thermal management in the near-infrared spectrum of smart windows, we introduce a configuration of amorphous Si–In–Zn–O (SIZO) /Ag/SIZO/NiO electrodes with varying thicknesses of SIZO on the top and bottom. This design aims to create electrochromic heat shutters for the dynamic regulation of solar radiation, utilizing sputtering technology for fabrication at room temperature. The engineered electrochromic heat shutter, with reduced SIZO bottom/top layer thickness, exhibits an outstanding visible modulation of 74 %, ensuring excellent visibility in windows, alongside remarkable near-infrared (NIR) shielding effectiveness of 68 % at 950 nm and 86 % at 2400 nm, a rapid switching speed of 0.5 s for bleaching and 0.8 s for coloration, higher charge intercalation, as well as commendable cycle stability. The Electrochemical impedance spectroscopy (EIS) confirmed the enhanced/faster ion transport inside the electrode matrix due to increased conductivity and a reduced diffusion barrier. With 519 Fg^{−1} specific capacitance, the capacitive electrochromic electrode has improved electrochemical kinetics, high charge capacity, and may be used as a secondary energy storage device. Our research finding may provide a major advancement in the development of electrochromic heat shutters, for developing energy-efficient smart buildings.

1. Introduction

The growing global population along with lightning-fast urbanization has led to a rise in energy consumption within buildings, particularly in air conditioning as well as ventilating systems used for lighting, cooling, and heating. This sector accounts for around 30–45 % of the world's energy usage [1,2]. Because of the significant rise in energy demands for the cooling and heating of buildings, it is essential to minimize energy consumption from these services while ensuring an adequate level of comfort within the buildings in order to promote sustainable development [3,4]. To address this challenge, the focus on technology-driven buildings and energy conservation has significantly increased over the past few years [5]. Smart windows have the capability to intelligently adjust the transmittance of solar irradiation, enhancing occupant comfort while also being envisioned as a means to conserve energy. The visible portion of solar radiation primarily influences the effectiveness of natural daylight within buildings. The other half of solar radiation consists of the near-infrared region (NIR).

Managing the amount of NIR light that passes through windows greatly affects the management of indoor temperatures and energy savings. Just a minor change of 1 degree Celsius in the interior temperature may result in a notable 10 % reduction in energy usage [6,7]. Several techniques exist to regulate solar transmission through a smart window, like electrochromism, [8] and low emissivity [9]. Electrochromic devices (ECDs) represent a distinct category of switchable devices that are triggered by electrical stimuli. Electrochromic smart windows are commercially available technology that adapts their optical properties in response to electrical stimuli. Low-emissivity (or "Low-E") glass is an energy-efficient material that keeps heat inside during cold weather and keeps heat outside during hot weather by efficiently blocking roughly 90 % of NIR radiation. Electrochromic glass integrated into smart windows, coupled with low-emissive properties, presents a promising approach for minimizing energy consumption in buildings [10].

The conventional and widely recognized configuration of ECD consists of a five-layer arrangement: electrode, ion storage layer, electrolyte, electrochromic layer, and top electrode [4]. So far, transition-metal

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oxides (TMOs), conducting polymers, and Prussian blue are the extensively studied electrochromic (EC) materials [11,12]. Among TMOs, nickel oxide (NiO) stands out as an extensively examined positive EC material due to its exceptional electrochromic efficiency [13].

The Transparent Conducting Oxides (TCO), which serve as the primary materials for the top and bottom electrodes of the ECD, must possess improved opto-electrical characteristics. TCOs are capable of injecting or collecting charge carriers without altering optical transmission. The wavelength-selection transmission mode of TCOs, resulting from the collective plasma excitation, enables their application on windows to reduce radiative thermal loss as well as to regulate solar gain [14]. At present, the most utilized transparent conducting electrode (TCEs), using TCOs are those made from indium tin oxide (ITO), which exhibit a transmittance exceeding 80 % in the visible range and an electrical conductivity greater than 10^4 S cm^{-1} [15]. Nonetheless, ITO necessitates elevated processing temperatures exceeding 250°C , exhibits fragility, and incurs significant costs for raw materials [16]. The fabrication of ultrathin metal placed between oxide films in oxide/metal/oxide (O/M/O) configurations is considered a promising strategy for achieving high-performance TCOs. O/M/O TCOs demonstrate several advantageous characteristics, such as remarkable stability in ambient conditions due to the encapsulation of the metal film by oxide layers, the capacity for deformation attributed to the ductile nature of the metal film, and the feasibility of large-scale fabrication at ambient temperatures on plastic substrates. NIR shielding can be achieved through fabrication methods as reported in literature [17,18]. Likewise, these OMO substrates also exhibit significant low-emissivity property which can shield the NIR radiation. The transmittance and the reflectance of O/M/O TCOs may be adjusted by changing the thicknesses of the top and bottom oxide materials [19].

This study presents a multilayer configuration comprising oxide-metal-oxide (OMO) fabricated with Si-In-Zn-O (SIZO) /Ag/SIZO layers, which serve as a transparent conducting electrode (TCE) material with low-e configuration termed as (LEOMO). The thickness of the top and bottom oxide layers was tailored to get optimum opto-electrical properties. TCO layers were prepared at room temperature which eliminates additional thermal process. The tailored TCO functions as a heat shutter with high optical transparency of 97 % at the visible range and 6.5 % at the NIR range. The primary goal of the investigation is to develop energy-efficient electrochromic heat shutters. Electrochromic NiO thin films were fabricated on OMO substrate at room temperature via RF sputtering. The engineered material exhibited exceptional electrochromic performance, achieving 74 % optical modulation in the visible spectrum and efficiently obstructing NIR radiation with a rapid switching speed of 0.5 s for bleaching and 0.8 s for coloration. In addition, it has remarkable cycle stability. The developed electrochromic heat shutters offer a viable approach for achieving energy savings throughout the year in both heating and cooling applications.

2. Experimental methods

2.1. Preparation of OMO Low-e TCE layer

Thin films of SIZO/Ag/SIZO multilayer were prepared through the multi-sputtering technique (DaeKi Hi-Tech). The amorphous oxide layer was prepared using RF magnetron sputtering with a Si-In-Zn-O target in which silicon was incorporated into an In-Zn-O system, whereas the Ag layer was formed under room temperature using DC sputtering with a 99.99 % pure Ag metal target. With an operating pressure at 6×10^{-3} Torr and an RF power of 40 W, SIZO layer depositions were performed for different deposition times of 30, 35, 40, and 45 min. For silver (Ag) deposition, DC sputtering parameters were 5×10^{-6} Torr base pressure, 20 W power, and 4×10^{-3} Torr working pressure.

2.2. Preparation of electrochromic layer

An ultra-pure nickel oxide target (99.9 %) has been used to deposit NiO thin film via the RF magnetron process. Initially, Argon (inert) gas was introduced into the chamber. The deposition was carried out at room temperature on an OMO substrate placed 17 cm from the target with a deposition pressure of 20 mTorr, and a rf power of 80 W.

2.3. ECD fabrication

We manually assembled the prototype ECD, which measures $3 \text{ cm} \times 3 \text{ cm}$ and exhibits a sandwich design (Fig. 1g). The SIZO/Ag/SIZO/NiO multilayer deposited on glass functions as the working electrode. An ultra-pure ITO target was used to deposit an ITO thin film onto a glass substrate using DC sputtering. The deposition occurred at ambient temperature under a pressure of 4 mTorr using an RF power of 30 W. The deposited ITO is subjected to post-annealing treatment at 350°C . The fabricated ITO thin film functions as a counter electrode. A spacer insulating frame is positioned between the two electrodes, providing both separation and facilitating encapsulation. A 2 M KOH electrolyte is filled between the working electrode and the counter electrode. All device construction procedures were conducted in an atmospheric environment. The device's performance was examined in a two-electrode setup in an atmospheric environment. Fig. 1(a-i) illustrates the schematic representation of ECD fabrication.

2.4. Measurements

Investigation of visible and IR transmittance of the OMO and EC layer was conducted using a UV-Vis optical spectrometer (Cary 5000 UV-Vis-NIR, Agilent) in the wavelength range of 300–2400 nm, while electrical parameters for OMO were examined using Hall measurement (HMS 3000, Ecopia). The surface morphology was investigated using Atomic Force Microscopy (AFM; Nanoscope:E). The cyclic voltammetry (CV), and Electrochemical Impedance Spectroscopy (EIS) of the film was studied using the EC system SP-300 potentiostat (Biologic Science Instruments, France) in conjunction with EC lab software. The chronocoulometry (CC), and chronoamperometry (CA) were performed using an electrochemical workstation equipped with a scanning potentiostat/galvanostat (CHI600E). Colouration and bleaching of devices were achieved by subjecting them to external voltages of +3 V and –3 V, respectively, using a DC source.

3. Results and discussion

3.1. Optical and electrical analyses of the SIZO/Ag/SIZO multiple layers

Low-e coating serves as a functional layer for window glass, exhibiting transparency in the visible light spectrum (380 nm–780 nm) while demonstrating high reflectivity in the infrared region, effectively minimizing heat loss through radiant heat [20]. Hence, the optical transmittance spectra measured in the Vis-IR wavelength region (300 nm–2200 nm) of the OMO sample with top and bottom oxide layers deposited at different thicknesses is shown in Fig. 2(a). The prepared samples deposited at 30, 35, 40, 45 mins were termed as heat shutters, HS1, HS2, HS3, and HS4. It can be observed that all the films show high optical transparency (more than 90 % in the visible region) and effectively block NIR radiation. As the thickness of the top and bottom SIZO layers increases, the maximum transmittance wavelength (λ_{MAX}) shifts towards longer wavelength regions (red shift). The resulting result may be elucidated by changes in the non-reflective state relative to the thickness of the top and bottom SIZO layers. The observed red shift may be attributed to the impact of several parameters, including light scattering effects [21], surface roughness [22], and the minor variations in n and k values with respect to the increasing thickness of the SIZO layer [23]. The transmittance measured at 550 nm and maximum

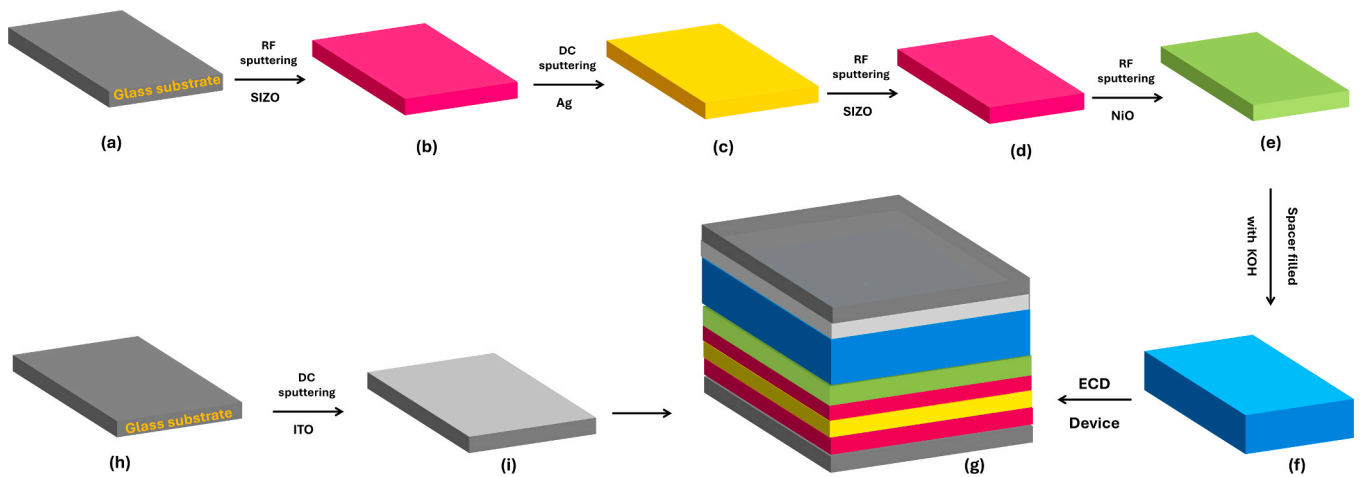


Fig. 1. Schematic illustration of Electrochromic Device fabrication.

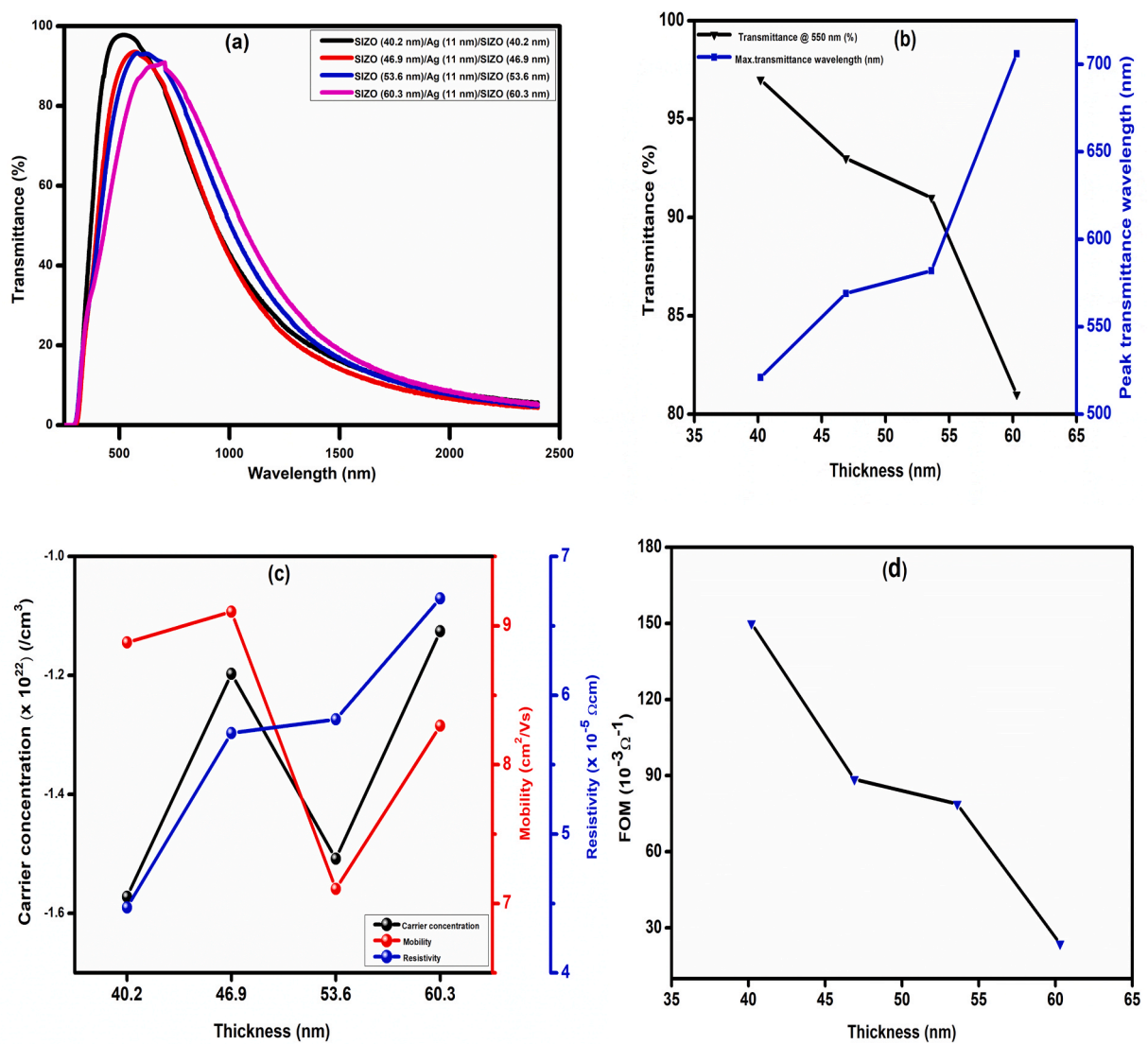


Fig. 2. (a) The transmittance spectra of SIZO OMO TCE as a function of SIZO layer thickness, (b) the optical transmittance at 550 nm and peak transmittance wavelength of SIZO OMO TCE as a function of SIZO layer thickness, (c) Carrier concentration, mobility and resistivity of SIZO OMO TCE as a function of SIZO layer thickness, and (d) figure of merit of SIZO OMO TCE as a function of SIZO layer thickness.

Table 1

Optical properties of SIZO OMO multilayers deposited on glass substrate.

Sample	SIZO bottom/ top layer thickness (nm)	Transmittance @ 550 nm	Transmittance @ 950 nm	Transmittance @ 2200 nm
HS1	40.2	97.37	48.31	6.58
HS2	46.9	93.15	48.18	5.39
HS3	53.6	91.41	57.41	5.92
HS4	60.3	81.91	64.38	6.45

transmittance is shown in Fig. 2(b). As shown in Table 1, the HS1 sample shows a high optical transparency of 97 % at 550 nm and a high reflectance of over 94 % at 2200 nm. Fig. 2(c) shows the electrical properties, like carrier concentration, carrier mobility, and resistivity with respect to OMO top/bottom layer thickness. The resistivity is found to increase while the carrier concentration and the mobility decrease with increasing thickness. The conductivity of the films having a thickness much less than the mean free path of electrons is mainly restricted by scattering that greatly decreases electron mobility [9]. Thus, the increase in resistivity with increasing thickness may be attributed to the increased scattering at the grain boundaries inducing reduced mobility. The HS1 sample showed very low resistivity and sheet resistance even without substrate heating or post-annealing treatment, making it suitable for the fabrication of highly efficient EC devices.

To ensure maximum device performance, it is essential to balance optical transmittance with the sheet resistance (R_s) of the TCE. The efficiency of a TCE may be assessed by determining the figure of merit (FoM) based on its electrical & optical characteristics [24].

$$\varphi_{TC} = \frac{T_{550nm}^{10}}{R_s}$$

Here T_{550nm} is the transmittance at 550 nm, and R_s is the sheet resistance. As shown in Fig. 2(d), the FoM decrease with increasing thickness due to increased sheet resistance. To highlight the performance advantages of the SIZO/Ag/SIZO multilayers a comparative analysis of the transmittance, conductivity, and Figure of Merit between the SIZO/Ag/SIZO multilayers, traditional ITO glass, and commercial Low-e glass is presented in Table 2. Hence, as given in Table 2 the optimum condition for efficient TCE is the OMO electrode deposited at 30 mins, HS1 sample.

3.2. Performance of TCE as electrochromic heat shutters

The crystalline structure and morphology of NiO films greatly influence their electrochromic characteristics. Our prior investigation [26] indicated that the XRD patterns of SIZO/Ag/SIZO multilayer and NiO films exhibited an amorphous characteristic. Amorphous thin films, characterized by their disordered structural arrangement, may promote many open spaces for ion transportation, enable rapid ion migration, and provide minimal energy barriers during ion insertion & extraction

Table 2

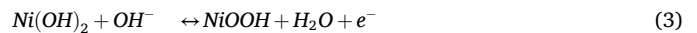
Comparative analysis on optical and electrical properties of SIZO/Ag/SIZO multilayers, traditional ITO glass, and commercial Low-e glass.

Sample	Transmittance @ 550 nm	Resistivity Ω cm	Figure of merit	Reference
HS1	97.37	4.47×10^{-5}	150	-
HS2	93.15	5.73×10^{-5}	88.6	-
HS3	91.41	5.83×10^{-5}	78.8	-
HS4	81.91	6.70×10^{-5}	23.7	-
ITO glass	80 % – 90 %	$\sim 10^{-3}$	$\approx 1-2 \times 10^{-3} \Omega^{-1}$	[15]
Commercial Low-e glass	60–75 %	$\sim 10^{-4}$	$\sim 2-5 \times 10^{-4} \Omega^{-1}$	[25]

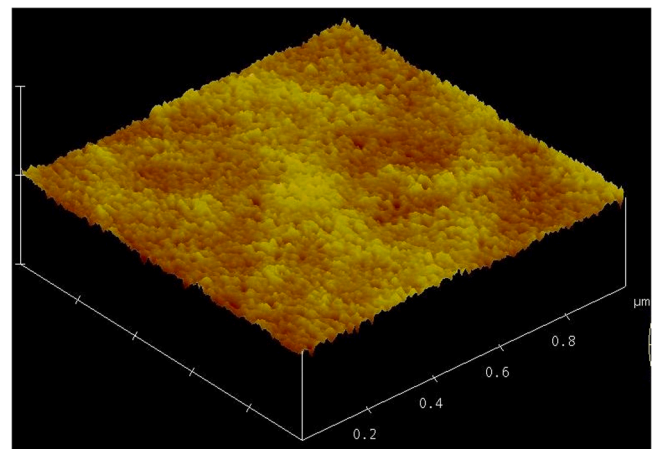
[27]. This structure minimizes the diffusion length for ions & increases the active specific surface area, leading to enhanced colouring efficiency and remarkable electrochromic characteristics [28]. The amorphous nature of NiO films showed better electrochromic efficiency than the crystalline NiO films cycled in KOH electrolyte [29]. Hence, our amorphous NiO film may promote the fast movement of electrolyte ions within the film, enabling a greater capacity for ion accommodation and improved optical modulation [30,31]. Fig. 3 shows the AFM image of the HS1 sample deposited on a glass substrate. The deposited film had a uniform surface devoid of pinholes. The development of small and isolated nuclear morphology has been observed. The root mean square (R_{rms}) roughness value of 0.632 nm was obtained, which is lower than the published R_{rms} values for NiO films [32–35], indicating a smoother surface and a less crystalline structure.

The electrochemical analysis of the heat shutters was examined using a conventional three-electrode electrochemical setup. The electrode configurations are as follows: Working electrode: OMO-NiO, counter electrode: Pt, reference electrode: Ag/AgCl, electrolyte: 2 M KOH. The cyclic voltammetry (CV) analysis performed at different scan rates, like 25, 50, 100, and 150 mV, for the NiO thin film deposited on OMO having different top/bottom layer thicknesses has been displayed in Fig. 4(a-d). The CV curves show two prominent redox peaks: an anodic peak at around 0.45 V and a cathodic peak at around -0.05 V with the applied potential of ± 1.5 V.

Initially, the pristine OMO-NiO electrode (light brown or translucent) may reversibly convert into $Ni(OH)_2$, resulting in the formation of a thin layer on its surface until equilibrium is reached as per Eq. (1) [36]. The electrochromic reaction of the OMO-NiO electrode in an alkaline solution may be represented by Eqs. (2) and (3) [37]. The coloring process involves the oxidation reaction from NiO and $Ni(OH)_2$ (transparent) to $NiOOH$ (dark brown) during charging, while the bleaching step entails the reduction reaction from $NiOOH$ (dark brown) back to NiO and $Ni(OH)_2$.



When the film is colored (a positive voltage is applied), electrons (e^-) are expelled, and NiO/ $Ni(OH)_2$ undergoes oxidation, while OH^- ions in the electrolyte are incorporated into the film to produce $NiOOH$, which exhibits a dark brown hue. Simultaneously, O_2 in the solution is converted to OH^- ions on the surface of the counter electrode when a negative voltage is supplied, so completing the coloring process. The electrons produced in this process will return to the positive electrode, so completing the electrode's charging process. Likewise, when the film

**Fig. 3.** AFM image for HS1 sample.

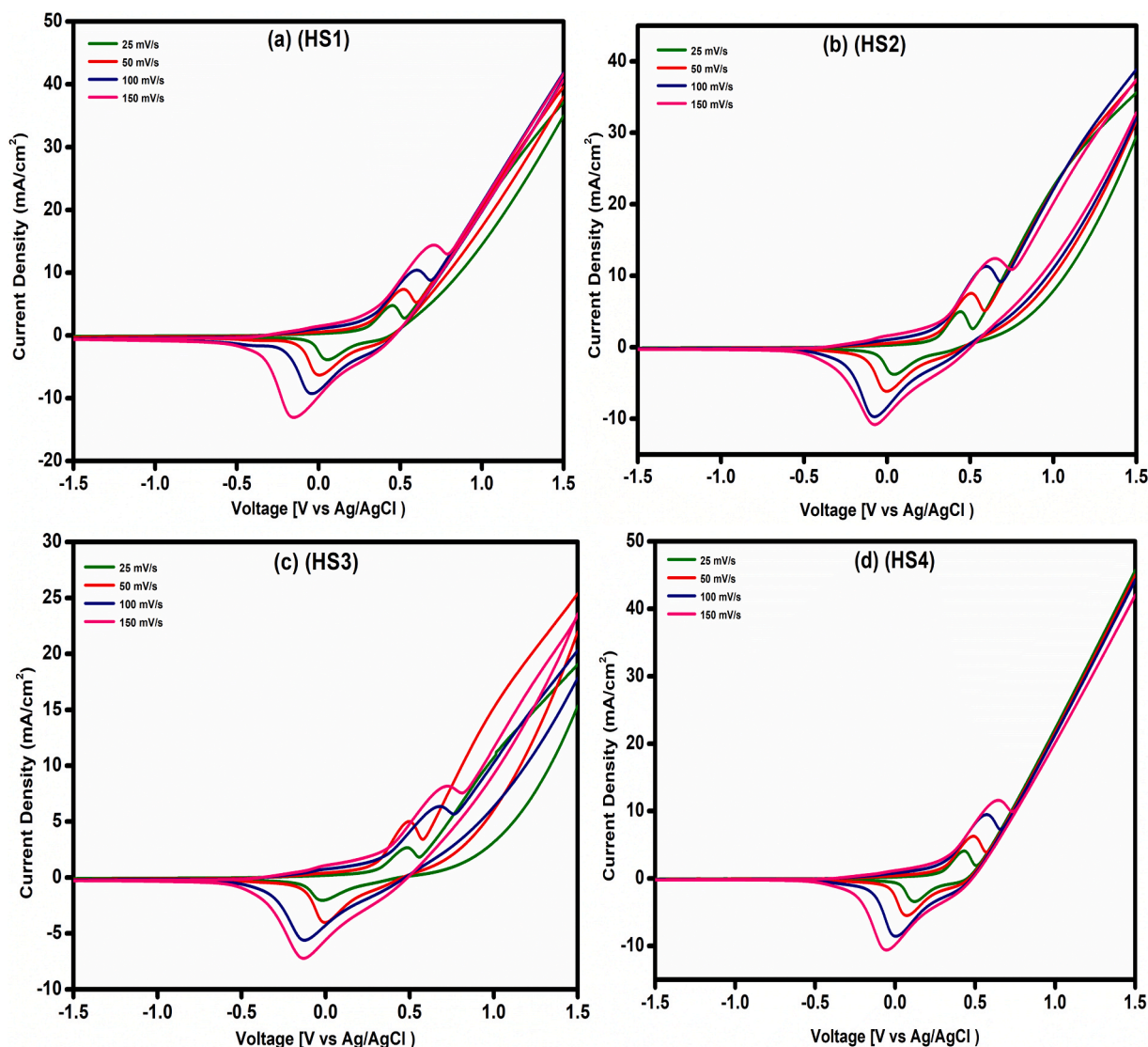


Fig. 4. CV studies for (a) HS1, (b) HS2, (c) HS3, and (d) HS4 thin films.

undergoes bleaching (a negative voltage is applied), electrons are gained, NiOOH is reduced by hydration, and OH⁻ ions are deintercalated from the film, resulting in the formation of transparent Ni(OH)₂ and NiO, as described in Eqs. (2) and (3). Simultaneously, OH⁻ ions in the electrolyte are oxidized to O₂ on the counter electrode surface when a positive voltage is provided, so completing the bleaching and discharging process of the NiO film [37]. Despite the widespread acceptance of the idea among researchers [36,37], several debates persist that need additional refinement and optimization.

Furthermore, redox peaks exhibit a symmetrical characteristic, indicating a robust intrinsic reversibility. The current density rises with an increase in scan rate, while all cyclic voltammetry curves have a consistent shape, indicating that the fabricated film promotes fast redox reactions. At high scan rates, the CV curve demonstrates enhanced symmetry, indicating a superior high-rate response. Additionally, the current and potential at the two redox peaks move towards the positive and negative axes, respectively, when the scan rate is increased. During the faradic redox process, ions and electrons diffuse rapidly across NiO thin films, which may explain the observed shift [38]. Fig. 4(a) illustrates that the HS1 sample exhibits significantly larger current densities and wider CV relative to the other samples. This signifies that in the HS1, electrons are readily transferred from the oxide layer to the metal layer, and vice versa. The reduced energy barrier between the OMO substrate

and the NiO layer facilitates the efficient transit of electrons or ions.

The electrochemical dynamics of NiO films have been investigated to acquire knowledge about the response rates among different states in the electrochromic films. The differentiation between faradaic and capacitive-controlled mechanisms could be ascertained by analyzing the CV results in accordance with the equation [39,40].

$$i = av^b$$

$$\log i_p = b \times \log v + \log a$$

where v signifies scan rate, and a and b are variables. The mechanism of ion insertion/extraction may be better understood if the value of b could be determined by analyzing the slopes of the curve by plotting $\log(i)$ versus $\log(v)$ (Fig. 5(a-d)). A value of b around 0.5 indicates a diffusion-controlled reaction, b near 1.0 signifies a capacitive process, & b within 0.5 and 1 denotes an integrated mechanism. As shown in Fig. 5(a-d) the derived b for all the samples lies between 0.6 and 0.7, indicating that the overall charge capacity is governed by both capacitor-like and diffusion-dominated processes.

Employing the formula that ensues, one can determine the capacity of the OMO-NiO electrode by determining the specific capacitance

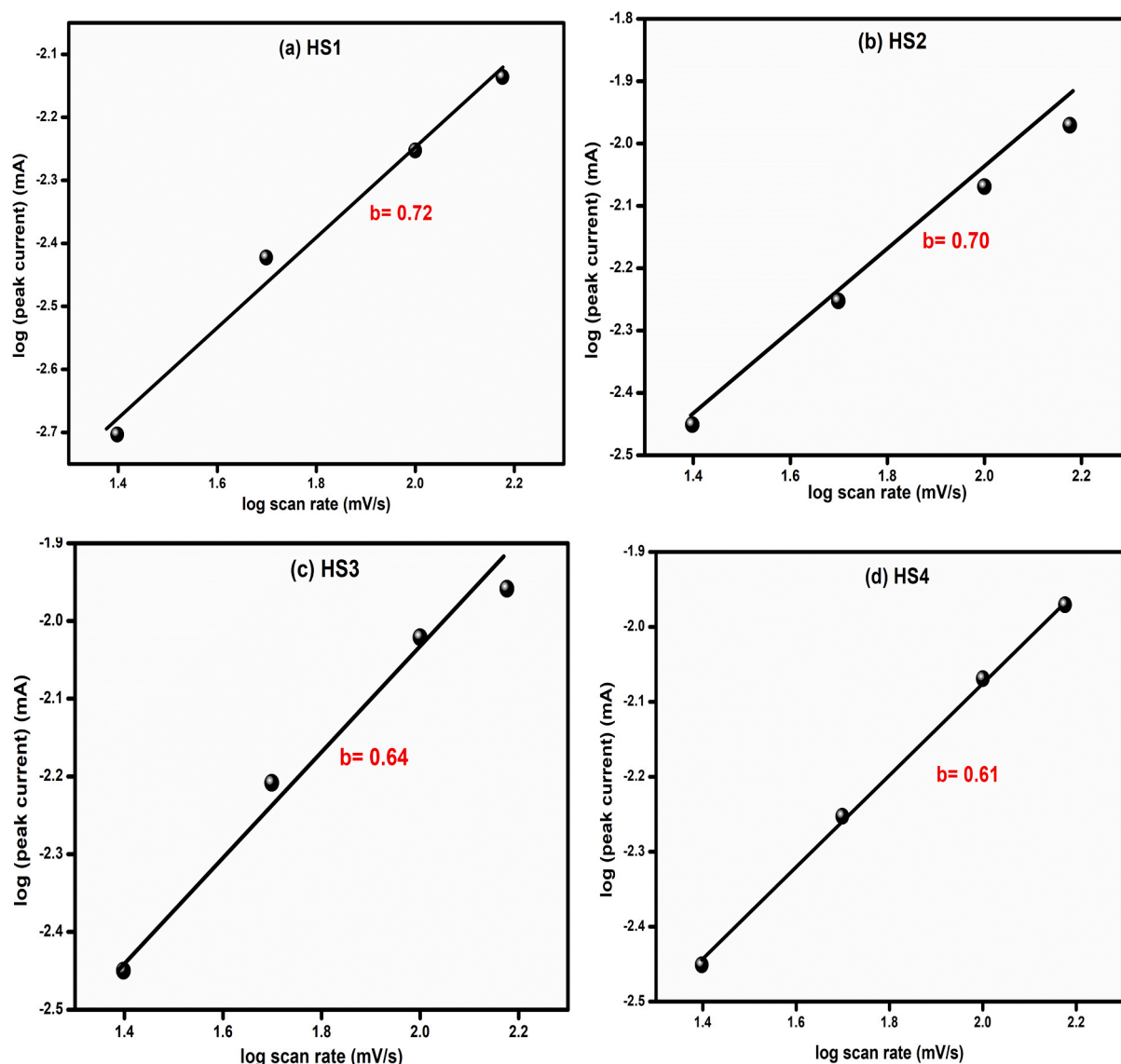


Fig. 5. log (i) against log (v) linear relationship for (a) HS1, (b) HS2, (c) HS3, and (d) HS4 thin films.

$$C_s = \frac{\int IdV}{\nu mV}$$

C_s specifies the specific capacitance of the working electrode (Fg^{-1}), I symbolizes the response current (A), ν marks the scan rate (mVs^{-1}), m corresponds to the mass of the active material, and V marks the applied potential window (V). Fig. 6(a) shows the correlation between calculated specific capacitance for OMO-NiO electrodes at a scan rate of 25 mVs^{-1} . The deposited film exhibits a maximum specific capacitance of 519 Fg^{-1} at a scan rate of 25 mVs^{-1} , surpassing previously reported values [41–46]. The specific capacitance diminishes with an increase in the electrode thickness, mostly due to fundamental electrochemical principles related to the constraints of electron kinetics & ion transport through the working electrode. Moreover, the HS1 sample shows higher specific capacitance. Generally, materials having high conductivity facilitate faster ion transport, improving the overall capacitance. Hence, HS1 showed higher specific capacitance due to the enhanced amount of electron transport & OH-ion diffusion into the electrode material. Conversely, higher OMO electrode thickness impedes electron dynamics & ion intercalation within the NiO material owing to its comparatively inadequate electrochemical as well as faradaic redox properties [47].

To further evaluate the impact of OMO top/bottom electrode

thickness on diffusion kinetics, the diffusion coefficients were determined using the Randles-Servcik equation:

$$i_p = 2.69 \times 10^5 \times A \times n^{3/2} \times D^{1/2} \times C \times \nu^{1/2}$$

Here, i_p denotes peak current (mA), A denotes working electrode area (cm^2), n denotes number of electrons transported, D denotes ion diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$), C denotes ion concentration ($\text{mol} \cdot \text{cm}^{-3}$), and ν denotes CV scanning rate ($\text{mV} \cdot \text{s}^{-1}$). The evaluated diffusion coefficient values for HS1, HS2, HS3, and HS4 samples are 3.10×10^{-11} , 1.55×10^{-11} , 7.75×10^{-12} , and $5.16 \times 10^{-12} \text{ cm}^2 \cdot \text{s}^{-1}$. The evaluated diffusion coefficient value decreases with an increase in the OMO top/bottom electrode thickness which is ascribed to the decrease of the ion insertion process [48]. HS1 had a superior diffusion coefficient, indicating an improved ion diffusion mechanism relative to the other samples. Effective diffusion kinetics need an uninterrupted clear channel for ions to traverse in both directions. The lower resistivity, or high conductivity of the electrode makes it highly suitable for the fabrication of highly efficient EC devices.

To examine the process of ion intercalation and deintercalation over time; Chronocoulometry was measured by applying the external voltage of $\pm 1.5 \text{ V}$ with a time interval of 5 s each. As shown in Fig. 6(b), HS1 sample showed higher amount of intercalated charge (Q_{in}) due to lesser

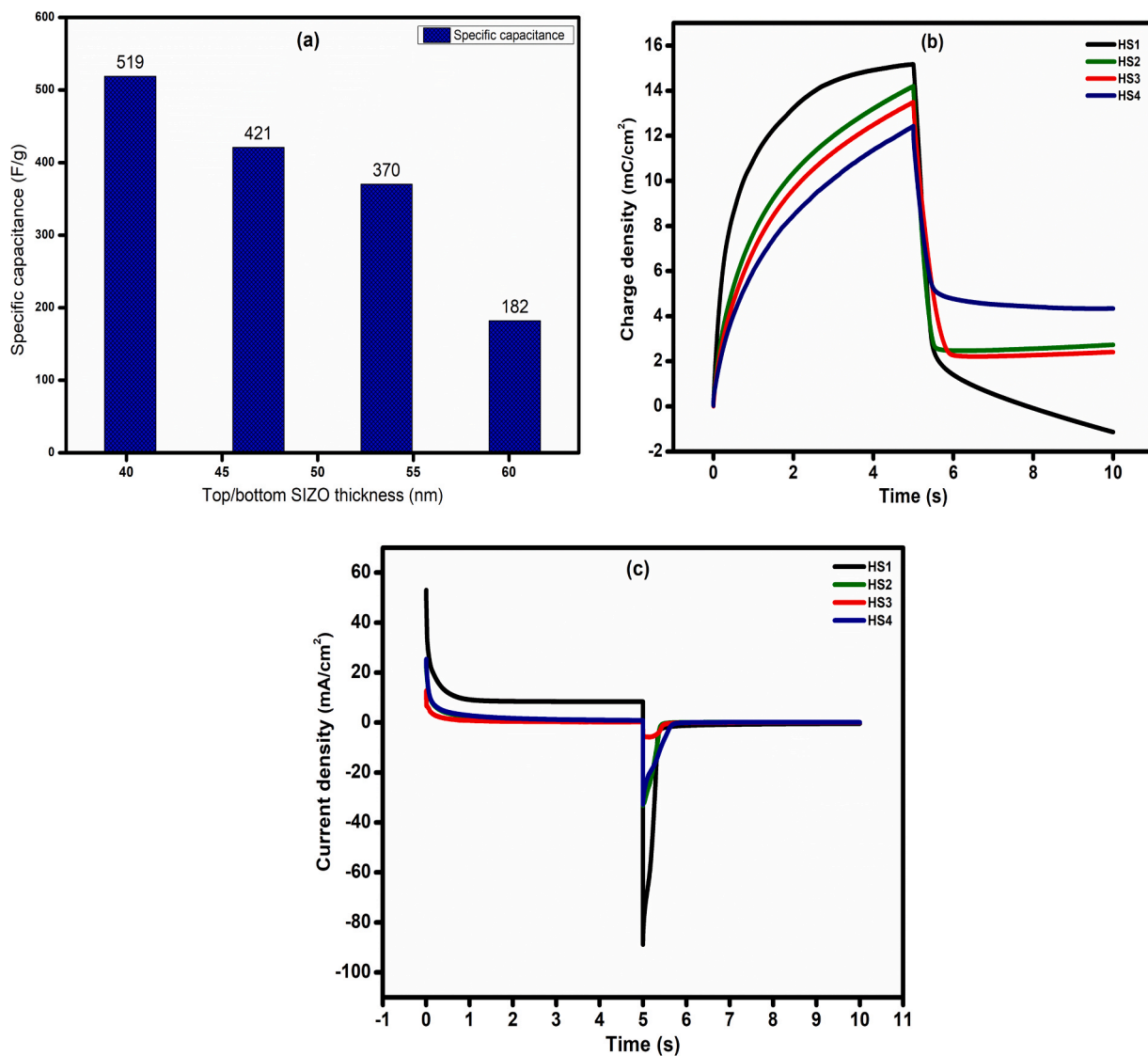


Fig. 6. (a) Relationship between specific capacitance and SIZO OMO electrodes as a function of SIZO layer thickness (b) Chronocoulometry curve of SIZO OMO- NiO electrode (c) Time response of the current density of SIZO OMO- NiO electrode.

Table 3

(a): Electrochemical properties of OMO-NiO electrode.

Sample	t_b/t_c (s)	R_{ct} (Ω)	Bleaching transmittance (T_b) (%) @ visible range	Colouring transmittance (T_c) (%) @ visible range	Optical modulation $\Delta T = (T_b - T_c)$ (%) @ visible range	Average visible optical modulation $\Delta T = (T_b - T_c)$ (%) @ (400–800 nm)	Average NIR optical modulation $\Delta T = (T_b - T_c)$ (%) @ (800–2400 nm)
HS1	0.5/0.8	2.6	80	6	74	59	16
HS2	0.6/0.9	14.15	80	12	68	49	9
HS3	0.9/1.1	1354	81	24	57	36	6
HS4	1.0/ 1.21	9910	74	22	52	36	5

(b): Electrochemical properties of OMO-NiO electrode

Sample	Optical density ΔOD @ visible range	Photopic contrast ratio (PCR) @ visible range	Color contrast CC (%)	Coloration efficiency CE (cm^2/C)
HS1	2.59	13.33	92.50	170
HS2	1.90	6.66	85.00	133
HS3	1.22	3.38	70.37	91
HS4	1.21	3.36	70.27	93

charge transfer resistance or high conductivity along with amorphous nature which favoured the easy intercalation of ions.

The significant dynamic response of the device is one crucial metric for evaluating the device performance. The response times (switching speed) of coloration (t_c)/bleaching (t_b) are defined as the time at which 90 % of the maximum transmittance contrast ($\Delta T_{\max}$) is achieved. [49]. The switching speed of the OMO-NiO electrode was measured using chronoamperometry study by applying the external voltage of ± 1.5 V with a time interval of 5 s each (Table 3 (a)). As shown in Fig. 6(c) and Table 3 (a) HS1 sample takes 0.8 s for coloration, whereas it takes ~ 0.5 s for bleaching. The increased switching speed displayed by HS1 when compared with other samples is due to the highly conductive nature of the OMO electrode and the highly disordered amorphous nature of NiO, which facilitates fast electron diffusion, enabling quick insertion and extraction of ions, hence reducing the switching time [18].

The faster switching kinetics of HS1 electrode have been confirmed using electrochemical impedance spectroscopy (EIS) in the frequency range of 10 mHz to 10 kHz. As shown in Fig. 7(a-d) the Nyquist plot for HS1, HS2, HS3, and HS4 electrode displays a semicircle in the high-frequency domain, which indicates the charge-transfer resistance (R_{ct}), followed by an inclined line in the low-frequency domain, signifying the diffusion of ions [50]. The most obvious difference is the size of the

semicircle that appears in the high frequency regime. For example, as shown in Fig. 7(a-d) and Table 3 (a), for HS1 electrode, the corresponding semicircle was reduced compared to other electrodes, indicating a lower charge-transport resistance. Also, the HS1 electrode exhibited a steeper slope in comparison to the other samples suggesting the enhanced/faster ion transport inside the HS1 matrix due to increased conductivity and a reduced diffusion barrier [51]. This inference is consistent with the chronoamperometry studies.

Optical transmittance analyses were conducted using a two-electrode configuration, applying a DC voltage of ± 3 V, with platinum serving as the counter electrode, KOH as the electrolyte, and the manufactured LEOMO-NiO as the working electrode. Fig. 8(a) shows the optical transmittance spectra in the colored and bleached states for HS1, HS2, HS3, and HS4 samples. The optical transmittance value in the visible region (typically between 520 and 550 nm) in the bleached (T_b), and colored (T_c) state is provided in Table 3(a). Also, the optical modulation ($\Delta T = T_b - T_c$) in the visible region, average optical modulation in the visible range (400–800 nm), and average optical modulation in the NIR range (800–2400 nm), are provided in Table 3(a). The HS1 electrode shows maximum optical modulation. Fig. 8(b) shows the optical transmittance spectra in the colored and bleached states for the HS1 sample with an inset picture showing the 3×3 cm OMO-NiO electrode

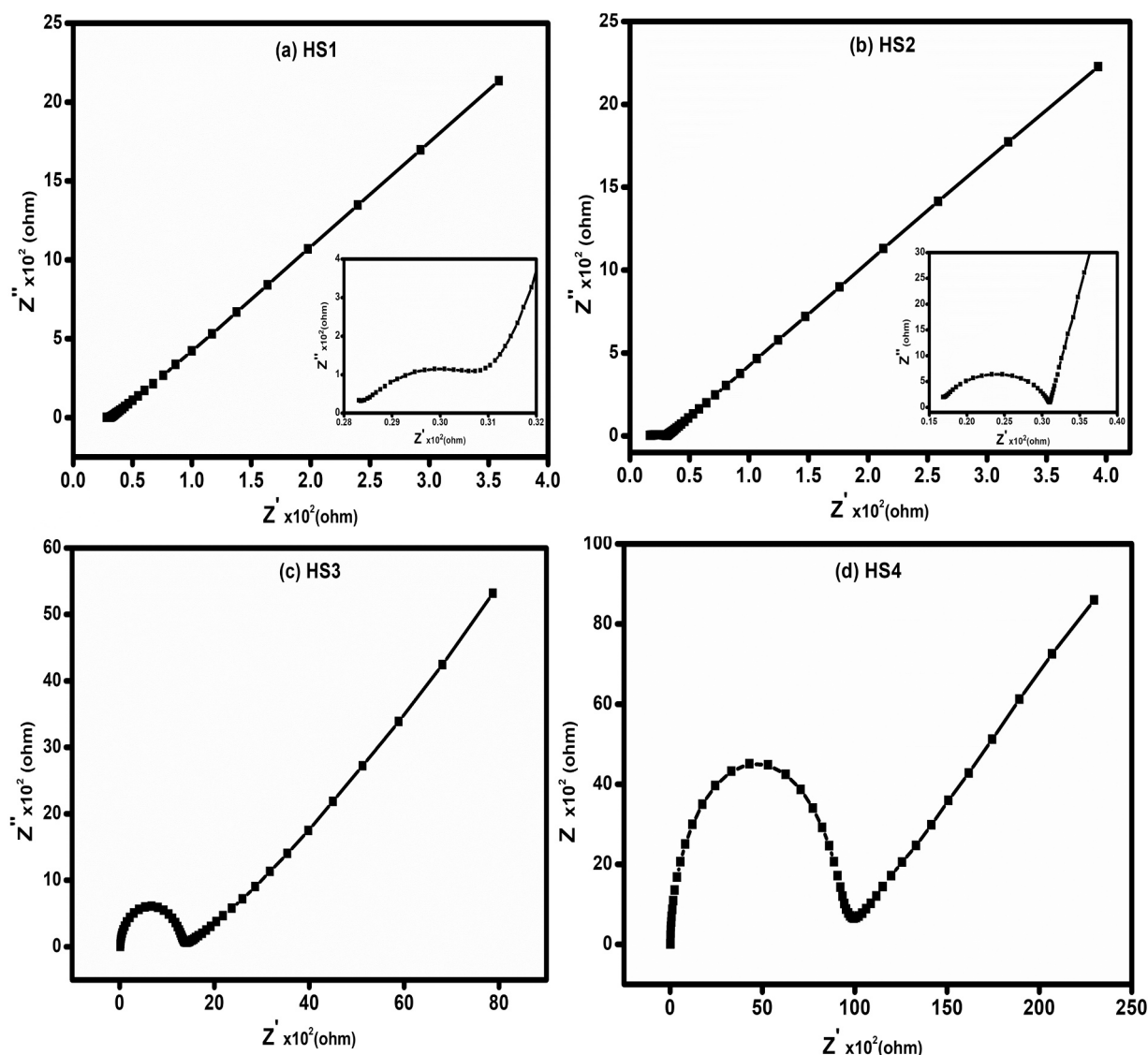


Fig. 7. Nyquist plot of (a) HS1, (b) HS2, (c) HS3, and (d) HS4 electrodes.

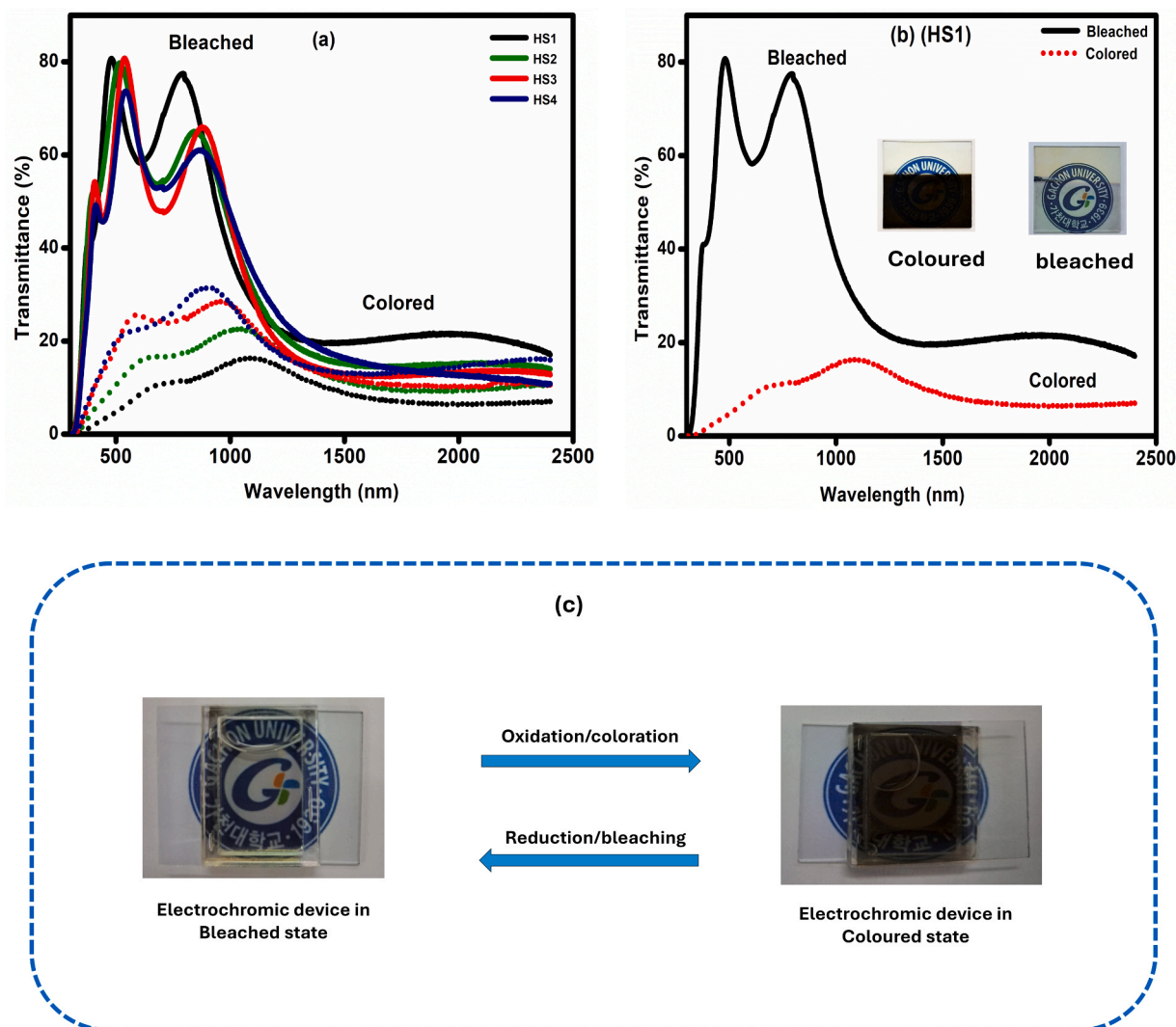


Fig. 8. (a) The transmittance spectra of HS1, HS2, HS3, and HS4 electrodes in the colored and bleached state, (b) Transmittance spectra of HS1 sample in the colored and bleached state with respective 3×3 cm sample in the inset, and (c) Fabricated electrochromic heat shutter device in the bleached and colored state.

in the colored and bleached states. Later a complete electrochromic heat shutter device (Fig. 8(c)) is fabricated by using OMO-NiO as the working electrode, ITO as the counter electrode, 2 M KOH as the electrolyte, and sealed properly. Fig. 8(c) shows the electrochromic heat shutter device in the colored and bleached states. Fig. 9(a-d) presents the schematic representation of the low-e electrochromic device with its corresponding window model both in dark and transparent modes. Typically, in summer, about 50 % of solar radiation that reaches a window is transported inside. Employing low-e electrochromic windows as a window layer would diminish internal heat transmission to 30 %, so facilitating the maintenance of cooler indoor conditions during summer while also providing great transparency for visible light. During winter, low-e electrochromic glass conserves interior warmth by preventing heat from leaving via the window and may act as a defroster to maintain window clarity when powered with DC voltage. Upon the application of a +3 V potential to the OMO-NiO film, it exhibits a dark mode (Fig. 9(a)), attaining a nearly black hue that obstructs 95 % of visible light and about 88 % in the near-infrared range (Fig. 9(b)). Consequently, the dark mode may significantly reduce the energy usage of the building for air conditioning and lighting. Upon reversing the potential to -3 V, the NiO film attains transparency (Fig. 9(c)), reaching 80 % throughout a wide frequency range within the visible spectrum, while effectively obstructing a significant portion of near-infrared (NIR) radiation (56 % at 950 nm and 93 % at 2400 nm) (Fig. 9(d)). Therefore, preserving

domestic warmth in winter by preventing the loss of interior heat to the outside environment and saving energy.

The color contrast (CC) for the OMO-NiO electrode was estimated using the following equation [18]:

$$\text{color contrast (CC)} = \frac{|T_f - T_i|}{T_f} \times 100\%$$

where T_f and T_i represents the transmittance (%) values corresponding to the final and initial transmittance, respectively. As shown in Table 3 (b), maximum color contrast of 92.5 % is observed for HS1 sample. The observed high color contrast in the case of the HS1 may be due to the low resistance, which helps more and faster diffusion of electrolyte ions [18]. In addition, the photopic contrast ratio (PCR) (T_b/T_c) is evaluated and given in Table 3 (b).

The coloration efficiency (η) was extracted using the following equation [52]

$$CE(\eta) = \frac{\Delta OD}{Q}$$

where ΔOD represents the optical density and Q denotes the total charge inserted/exerted per unit area when the device exhibits the change in the optical density. As shown in Table 4 the HS1 electrode showed higher coloration efficiency compared to other samples and the reported

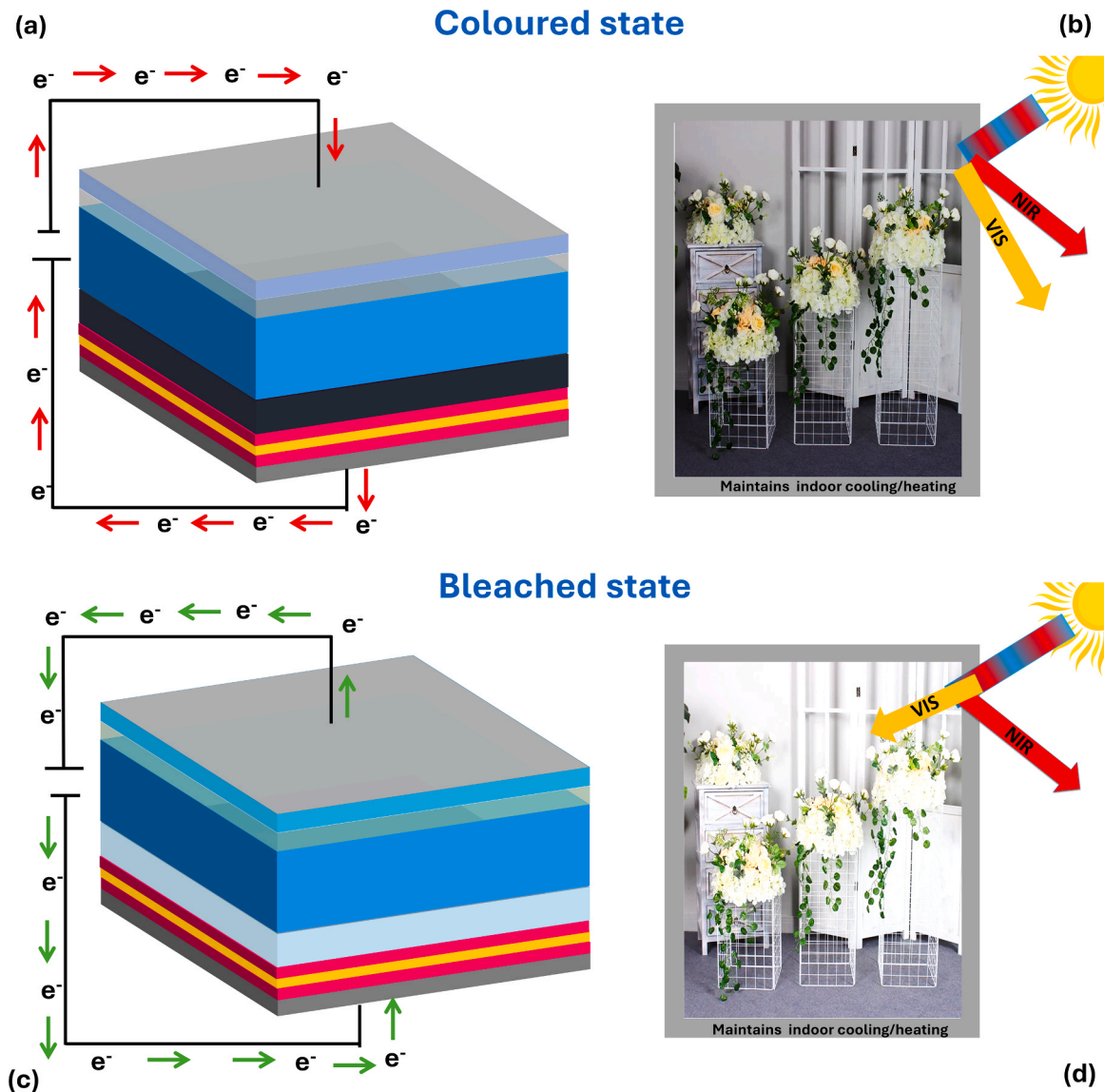


Fig. 9. The schematic illustration of a) electrochromic heat shutter device with OMO-NiO as cathode in the dark mode, (b) electrochromic heat shutter window in dark mode, (c) electrochromic heat shutter device with OMO-NiO as cathode in the transparent mode, and (d) electrochromic heat shutter window in transparent mode.

Table 4
The material, preparation method, and electrochromic properties of the NiO electrodes.

Material	Preparation method	Optical modulation (%)	t_b/t_c [s]	CE [$\text{cm}^2 \text{C}^{-1}$]	Cycle stability [cycle/times/%]	Electrolyte	Refs.
NiO	magnetron sputtering	51	2.1/4.9	23.7	1000/-	1 m LiOH	[53]
NiO	magnetron sputtering	54.7	1.7/7.0	—	—	0.1 m KOH	[54]
Ta-doped NiO	magnetron sputtering	56.4	19.88/28.01	15.54	1000/-	0.1 m NaOH	[55]
NiO	magnetron sputtering	65.1	1.3/1.4	39.3	500/71.7	1 m PC-LiClO ₄	[56]
NiO ₂ O	chemical bath deposition	30.3	2.58 /21.22	48.4	4000/87.4	0.5 m PC/LiClO ₄	[57]
NiO	e-beam evaporation	40.6	3.1/5.5	-	2000	0.5 M acetic acid	[58]
NiO	e-beam evaporation	91.8	4.1/5.3	167.96	8000	1 M PC/LiClO ₄	[59]
NiO	hydrothermal method	74.7	7.2/3.8	-	500	0.5 m L ⁻¹	[60]
SIZO/Ag/SIZO-NiO	magnetron sputtering	74	0.5/0.8	171	150	ZnSO ₄ 2 m KOH	This work

values [53–60].

Compared to other samples, HS1 demonstrated larger optical modulation of 74 % at 550 nm (visible), 32 % at 950 nm (near-infrared), and

14 % at 2400 nm (near-infrared). A crucial feature that establishes the long life of electrochromic devices is their cycle stability. The cyclic stability of the OMO-NiO electrode in 2 M KOH electrolyte was

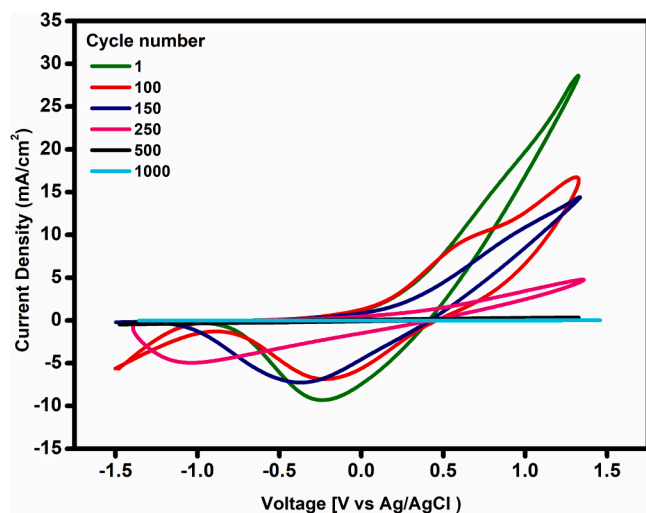


Fig. 10. Cyclic stability study for the HS1 sample.

examined for 1000 cycles. Based on Fig. 10, the current values started to decline after 150 cycles and continued to decline until 500 cycles. The diminution in peak current with the increase in CV cycles is due to the degradation of the OMO-NiO electrode [37]. The low-density Ni (OH)₂ reacts with water molecules during oxidation, leading to degradation from hydration. The degradation of NiO in aqueous electrolytes is associated with the partial dissolution of low-stability NiOOH during oxidation, together with ensuing self-discharge [61].

4. Conclusion

In conclusion, we devised a room temperature electrochromic heat shutter electrode for the making of electrochromic devices (ECDs). A multilayered OMO structure, consisting of SIZO/Ag/SIZO layers with varying thicknesses of the SIZO bottom/top layers, was manufactured at room temperature by employing the sputtering procedure as a TCE material. All TCE films exhibit optical transparency over 90 % in the visible spectrum and efficiently obstruct NIR light. As the thickness of the top and bottom SIZO layers grows, the maximum transmittance wavelength (λ_{MAX}) exhibits a red shift, likely due to scattering effects. TCE with a lower thickness of the top/bottom SIZO layer showed excellent electrical properties with a better figure of merit. At ambient temperature, NiO thin films were deposited on an OMO multilayer. The AFM image of the HS1 sample exhibited a homogeneous surface free of pinholes, with an R_{rms} value of 0.632 nm, indicating a smoother surface. The electrochromic heat shutter exhibited exceptional electrochromic efficiency, achieving optical modulation of approximately 74 %. It also displayed impressive near-infrared (NIR) shielding performance, reaching 68 % at 950 nm and 86 % at 2400 nm, coupled with notable cycle stability. The engineered electrochromic heat shutters provide a cool interior the summer and a warm environment during the winter, facilitating pleasant indoor conditions and unobstructed exterior visibility. The electrode deposited at lower thickness showed higher charge intercalation with rapid switching speed of 0.8 s for coloration and ~ 0.5 s for bleaching due to the highly conductive nature of the OMO electrode and the highly disordered amorphous nature of NiO. The smaller semicircle with a steeper slope in EIS study confirms the enhanced/faster ion transport inside the electrode matrix due to increased conductivity and a reduced diffusion barrier. The capacitive electrochromic electrode, exhibiting a specific capacitance of about 519 Fg⁻¹ for the HS1 sample, provides improved electrochemical kinetics and substantial charge capacity and is suitable to be employed as a secondary battery device. Therefore, we anticipate that the developed electrochromic heat shutters, which can be used as thermal envelopes in building walls, will offer a viable solution for achieving energy

efficiency throughout the year.

CRediT authorship contribution statement

Sang Yeol Lee: Writing – review & editing, Validation, Supervision.
J. Vivekanandan: Writing – original draft, Investigation, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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