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G. Srinivas, V. Sankaranarayanan, and S. Ramaprabhu*

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Optical switching properties of RCo₂-type alloy hydride based solid state device

G. Srinivas,^{1,2} V. Sankaranarayanan,¹ and S. Ramaprabhu^{2,a)}

¹Low Temperature Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai-600 036, India

²Alternative Energy Technology Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai-600 036, India

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The optical switching properties of a solid state device based on Ho_{0.6}Mm_{0.4}Co₂ (HMC) alloy thin film as a switching active layer, water pretreated Nafion membrane as a solid electrolyte, and a transparent conducting indium tin oxide (ITO) as a counterelectrode are investigated. The device is simple and has a reduced layer sequence of HMC/Pd/Nafion/ITO. The reversible optical switching of this device has been studied during electrochemical galvanostatic charging-discharging as well as cyclic voltammetric measurements. Further, the optical switching durability of the device has been tested by repeated electrochemical hydrogenation-dehydrogenation, and the variations in the optical switching properties are discussed. The special characteristic of the device is that it can reversibly switch between a metallic reflecting state and a semiconducting transparent state by a small reversible applied current/voltage indicating the potential substitution for conventional electrochromic devices. © 2008 American Institute of Physics. [DOI: 10.1063/1.2965189]

I. INTRODUCTION

The discovery of the reversible optical switching of yttrium and lanthanum thin films by Huiberts *et al.*¹ in 1996, upon reversible hydrogen absorption, triggered extensive studies on the rare earth (R) alloy hydride films.^{2,3} Later it has been demonstrated that R-Mg and Mg based alloy hydrides can switch reversibly from a reflecting state to a transparent state upon hydrogen absorption-desorption.⁴⁻⁹ These switching properties are mainly attributed to the reversible transformation from the metallic state of the host material to the semiconducting or insulating state upon hydrogen absorption. This issue has been the focus of attention due to prospects for technological applications. The electrochemical switching has then been successfully carried out in alkaline solutions under electrochemical polarization.¹⁰ Technologically, however, for most applications, the solid state device is more desirable because it prevents sealing problems and is also simple and easier to handle. Such a device, with a GdMg hydride layer as an active electrode and a hydrided zirconium oxide layer and a WO₃ layer as electrolyte and counterelectrode, respectively, has been demonstrated.^{11,12} Mercier and van der Sluis¹³ demonstrated a symmetric-GdMg based switchable solid state device with a complex layered sequence as follows: a GdMgH_x/Pd bottom electrode, a ZrO₂·(H₂O)_x·[H]_y electrolyte, and a Pd/GdMgH_y/Pd storage top electrode. Tajima *et al.*¹⁴ designed a solid state switchable mirror with the layer sequence Mg-Ni/Pd/Ta₂O₅/WO₃/indium tin oxide (ITO). These devices were constructed with extensive layer stacks and were composed of two anodic and cathodic electrochromic (EC) materials. Mg-alloy thin films were chosen for the anodic EC

materials and WO₃ thin films were chosen for cathodic EC materials.¹⁵ Further, the device performance was largely dependent on the characteristics of Ta₂O₅ or ZrO₂·(H₂O)_x·[H]_y electrolyte. The mechanism of the ion conductivity of the Ta₂O₅ film is very complex and seems to be closely related to crystal structure, oxygen vacancy, conduction route, etc. For practical use, it is important that the film has good proton conductivity. Further it was also largely dependent on the thickness, density, and preparation methods of Ta₂O₅ thin films.^{16,17} Thus for technological applications, one has to look for good solid proton conductors and a simple device which can operate reasonably with reduced layer stacking and lower voltage/current. Very recently, the hydriding-dehydriding, thermodynamic, structural, transport, and optical properties have been studied for the RCo₂-type R_{1-x}Mm_xCo₂ (R=Ho,Tb)-hydrogen system¹⁸⁻²¹ (Mm is an Indian mischmetal, a natural mixture of light rare earth metals containing 50 wt % of Ce, 35 wt % of La, 8 wt % of Pr, 5 wt % of Nd, 1.5 wt % of other rare earth elements, and 0.5 wt % Fe). Mm has been used mainly for economical reasons because it is produced directly from the ore without a costly rare earth separation.²² The Ho_{1-x}Mm_xCo₂ alloys show very fast hydriding kinetics¹⁹ and better diffusion properties with increasing Mm content.²³ The electrical resistivity of the hydrides of Ho_{1-x}Mm_xCo₂ alloys in the temperature range of 25–300 K exhibits gradual disappearance of magnetic transitions and thermally activated semiconductinglike behavior with increasing hydrogen concentration.²⁰ This thermally activated conduction strongly depends on the Mm concentration and more pronounced in the Ho_{0.6}Mm_{0.4}Co₂-H_y (HMC-H_y) system. The semiconducting behavior at higher hydrogen concentrations is mainly attributed to the strong electron-electron correlations. This has stimulated us to investigate the optical properties of the hydrogenated Ho_{0.6}Mm_{0.4}Co₂ (termed as HMC) thin films. In

^{a)}Author to whom correspondence should be addressed. Electronic mail: ramp@iitm.ac.in. FAX: +91-44-22570509. Tel.: +91-44-22574862.



FIG. 1. (Color online) Photograph of a solid state optical switching device ($10 \times 10 \text{ mm}^2$) in a (a) transparent hydrided state and (b) reflective dehydrided state.

In this present study, we present the switchable optical properties of a simplified solid state device based on a Pd covered HMC alloy thin film as active switching electrode, a transparent and conducting ITO film as counterelectrode, and a polymer Nafion membrane as a solid electrolyte. Polymer Nafion is an excellent and well known “solid” proton conductor widely used in proton exchange fuel cells. The reversible optical switching of this device has been measured simultaneously by measuring the electrode transparency during electrochemical galvanostatic charging-discharging as well as cyclic voltammetric measurements.

II. EXPERIMENTAL

An optical solid state device which can be switched electrochemically consists of two electrodes separated by an ion-conducting solid electrolyte.^{24,25} The polymer Nafion® 117 membrane (DuPont, USA) is used for ion-conducting solid electrolyte. This membrane must be solvated (by water or other small molecules) to start conducting. The Nafion membrane is equilibrated in de-ionized water for at least 30 min. Thus the solvated polymer Nafion membrane acts as a hydrogen storage layer and proton conductor.^{24,25} In this present device, the first electrode is comprised of a HMC/Pd film. The transparent ITO is used as a second electrode. Water pretreated Nafion membrane is sandwiched between these two electrodes with paper clips. The arrangement and photograph of the device are shown in Fig. 1. The layer sequence in the device is as follows:

Glass substrate |HMC|Pd| water pretreated Nafion

|ITO| glass substrate.

HMC (about 200 nm) thin film was deposited on the glass substrate using e-beam evaporation in high vacuum from the HMC alloy ingot.²¹ The film is covered with a thin (about 10 nm) Pd layer both to protect the film against oxidation and to catalyze the hydrogen uptake. An ITO film of about 250 nm was sputter deposited on a clean glass substrate. The as-deposited HMC/Pd films were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The compositional analysis was carried out using the energy dispersive analysis of x rays in a SEM.^{21,26} The weak reflections in the XRD patterns indicate either an amorphous or nanocrystalline nature of as-deposited HMC/Pd film (Fig. 2). SEM and AFM images of the HMC/Pd film reveal the uniform surface morphology [Figs. 3(a) and 3(b)]. The thin film composition is slightly different from the alloy ingot target material.

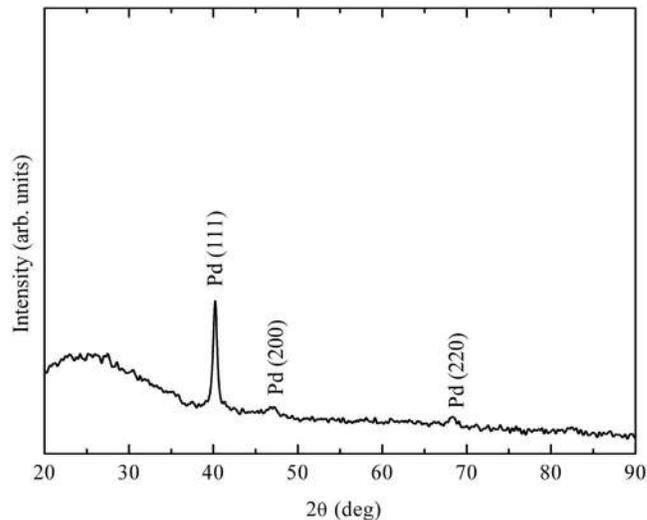


FIG. 2. XRD pattern of a Pd covered (10 nm) HMC thin film (200 nm).

However, this type of alloy even with the large deviations from the stoichiometric composition usually shows the same structural and phase behavior.²¹ Therefore throughout the

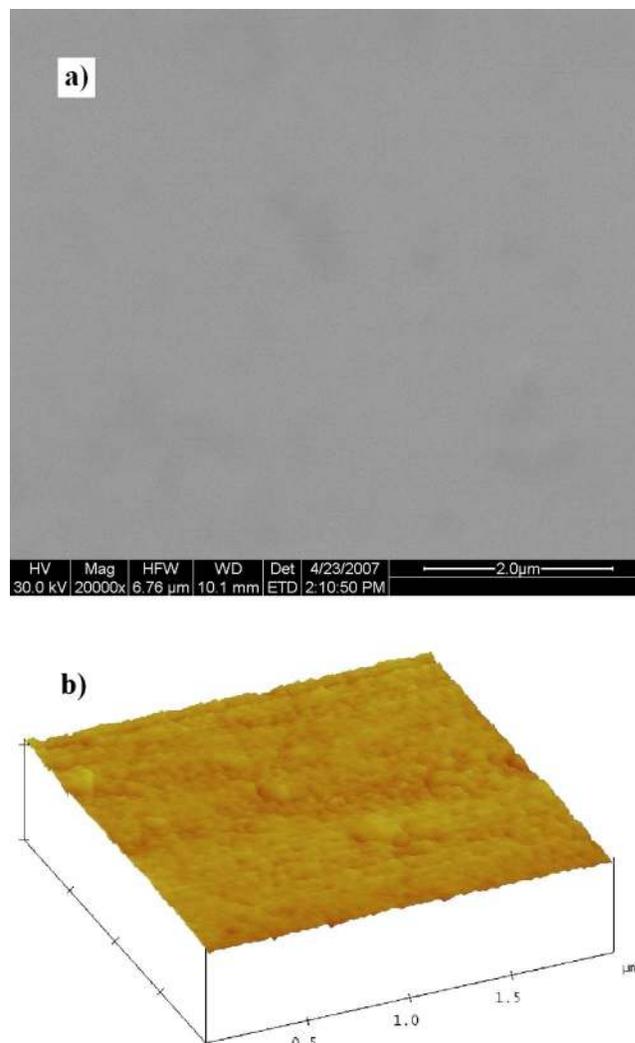


FIG. 3. (Color online) Surface morphology of a Pd covered HMC thin film. (a) SEM image and (b) AFM image.

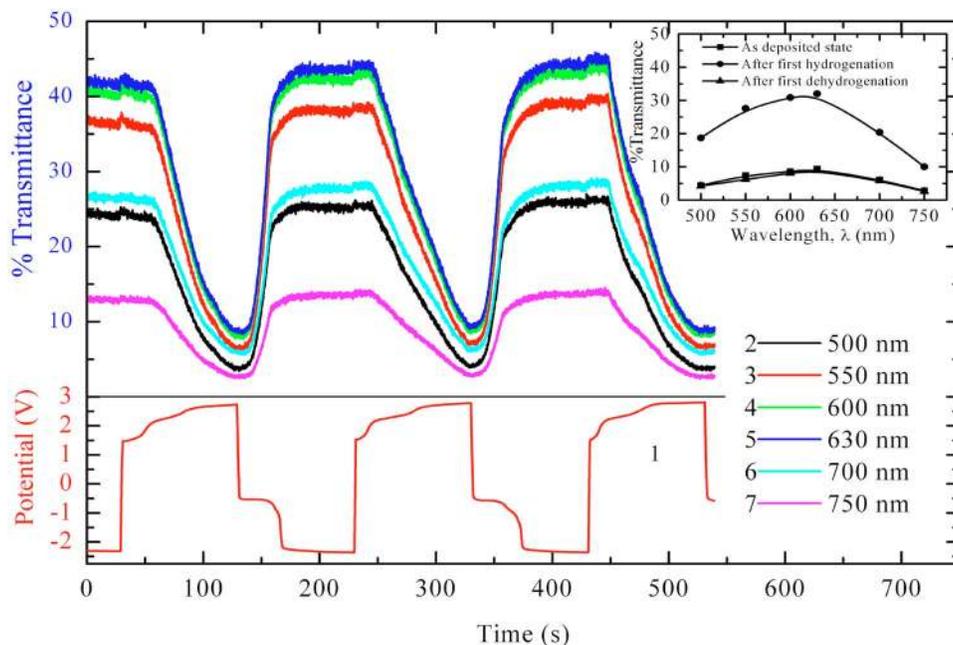


FIG. 4. (Color online) The optical transmittance of a solid state switching device during charging-discharging with a constant charging current of -0.5 mA for 100 s and discharging current of $+0.5$ mA for 100 s. (Inset) The transmittance against wavelength plot for the as-deposited state, the state after the first hydrogenation, and the state after the first dehydrogenation of the device.

manuscript, we use the thin film composition as an alloy ingot composition (HMC). The electrochemical experiments were performed using the Autolab 30 potentiostat/galvanostat. The optical transmittance of the device was measured by illuminating the device and detecting the light intensity using a white light source (DH 2000, Mikropack) and a spectrometer (USB2000, Ocean Optics) with the help of a fiber optic cable. The operational band of the spectrophotometer is in the range of 250–800 nm. The samples have a shiny metallic surface in the as-deposited state with 80% reflectance.

III. RESULTS AND DISCUSSION

Figure 4 shows the change in transmittance of the device during galvanostatic charging-discharging with a constant anodic and cathodic current of $+0.5$ and -0.5 mA, respectively, for the fourth, fifth, and sixth consecutive cycles. The current has been kept constant in each direction for 100 s. The measured potential response as a function of the time is represented as curve 1 in Fig. 4. The device is a two-electrode system and the measured potentials are cell potentials. Curves 2–6 represent the switching optical transmission of the device at different wavelengths of the illuminated white light for the corresponding charging-discharging cycles. The maximum transmittance occurs at 630 nm. During charging the electrode HMC film, OH^- ions, and H_2O are transferred through the Nafion membrane (electrolyte), and H_2O is reduced at the HMC film. By this electrochemical reaction, HMC is converted to HMC-H_y (hydrogen-rich semiconducting state where $y \approx 3.5$).²⁰ The electrode potential during charging behaves similar to that of hydrogen absorption pressure-composition isotherms of the HMC alloy.¹⁸ The electrode potential transient curve shows a more or less constant plateau at $V = -0.53$ V during the first few seconds and a steep increase toward more negative potentials at the end of charging followed by a leveling off when hydrogen gas evolution starts. The transmittance of the device

changes from $\sim 2\%$ to $\sim 45\%$ within about 50 s. The transparent state of the device is shown in Fig. 1(a) where we can see the back side. When a positive current is applied to the HMC- H_y film, it loses hydrogen and the device becomes mirrorlike and nontransparent [Fig. 1(b)] within about 80 s, which is a somewhat slower process than the charging state. The inset of Fig. 4 shows the transmittance against the wavelength plot for the as-deposited state, the states after the first hydrogenation and the first dehydrogenation of the device. The maximum transmittance after the first hydrogenation is about 30% and the recovered transmittance is just the same as the initial level. However, initially two to three cycles are necessary to activate the device, where the maximum obtainable transmission ($\sim 45\%$) reached within the first two hydrogenation and dehydrogenation cycles.

The cyclic switching is carried out to investigate the switching durability of the device. Figure 5 represents the switching durability of the device. This test is carried out by repeatedly applying a current of 0.5 mA for 100 s followed by -0.5 mA for 100 s. It can be seen that the maximum transmittance (at 630 nm) of the device gradually reduced within the first few cycles from about 45% to 20% without changing the switching speeds. Similarly, Mg–Ni based solid state devices with a Ta_2O_5 electrolyte^{14,17} showed a drastic drop in the maximum transmittance within a few initial subsequent switching cycles. After 50 switching cycles, the device maximum transmittance dropped from 40% to about 25%. After 100 switching cycles, the device showed transmittances of 5% and 19% at the reflective and transparent states, respectively. These results were interpreted with the degradation of the optical switching layer of Mg–Ni.¹⁷ However, in this present case, the initial drop in the maximum transmittance of the device is mainly attributed to the drying of water pretreated Nafion solid electrolyte. The optical switching of the switching film takes place with hydrogen. The transmission of the switching film is governed by the hydrogen content; transmission increases as hydrogen con-

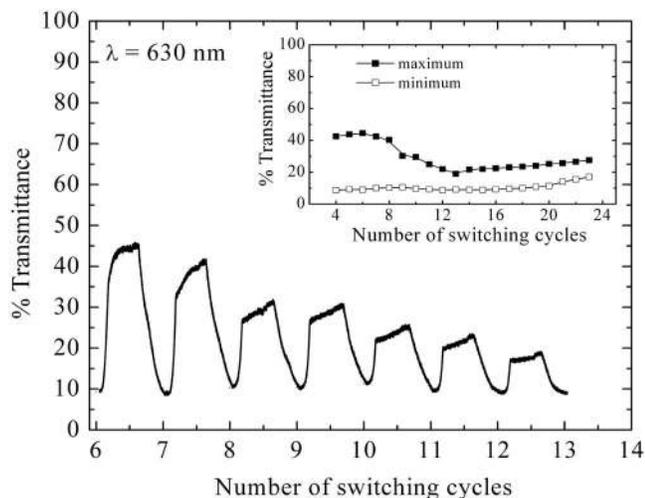


FIG. 5. The cyclic dependence of the optical transmittance of a solid state switching device with a constant current of ± 0.5 mA for a cyclic time of 200 s. (Inset) The maximum and minimum transmittances of the device for corresponding switching cycles.

tent increases. Thus the transmittance of the device is directly related to the availability of H^+ ions to the active electrode. The electrolyte Nafion membrane acts as a hydrogen storage layer and a solid proton conductor.^{24,25} In a dry state, the polymer ion-exchange membranes are not conductive. Thus the drying of the solvated Nafion membrane leads to the reduction in the H^+ ion supply to the active electrode. Consequently the hydrogen content in the active material will be reduced. Since the transparency of the metal hydride thin films is directly related to the absorbed hydrogen concentration, the device shows the reduction in the maximum possible transmittance. Matveeva *et al.*²⁴ employed Y/Pd cathode and the ITO anode separated by a Nafion membrane, which was equilibrated in water or other solvents for at least 30 min, and found that the device was operable only for a short time due to the drying of the membrane. However, in the present work, this transmittance state continues with longer switching cycles (Fig. 5). Further, we believe that an appropriate solvent with higher viscosity and low volatility in the Nafion membrane and proper thickness of the Nafion would prevent the early drop in transmittance of the device and improve switching durability. The inset of Fig. 5 shows the gradual increase in the maximum and minimum transmittance levels with subsequent switching cycles. Since the hydrogenated RCO_2 -type materials are thermodynamically more stable in nature,^{18–20} it is mainly assumed that the small amount of the hydrogen remain in the optical switching HMC material. The hydrogen content gradually increases during the cyclic test. Similar behavior was observed in the Mg–Ni based solid state switchable optical device¹⁴ in which the authors think that the proton remained behind in the optical switching layer gradually during the cyclic test. Thus, the remaining hydride state was maintained in the Mg–Ni layer, and the device was not able to show a complete reflective state. Therefore, the minimum transmittance became large.

The optical and hydriding-dehydriding properties of the device have been investigated further by the dynamic

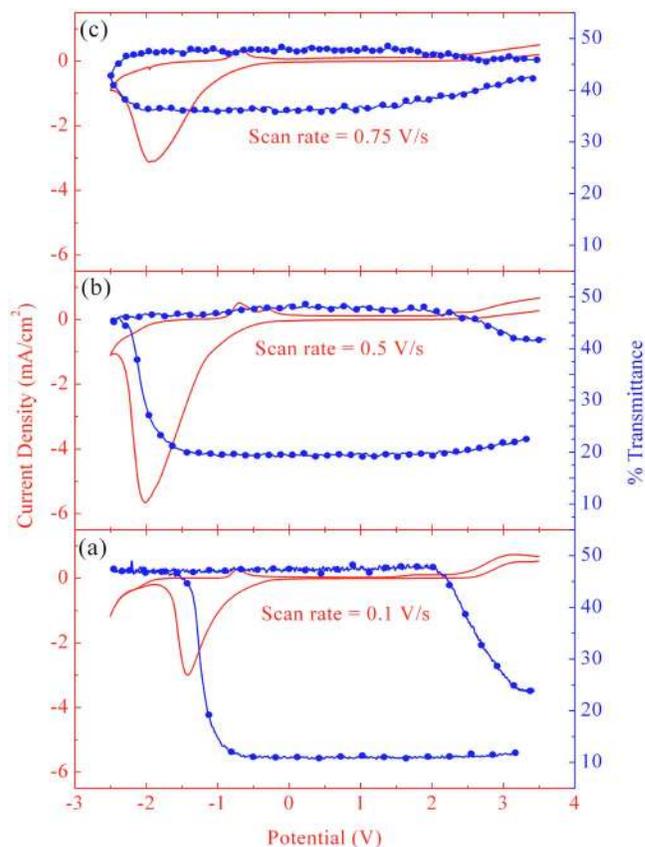


FIG. 6. (Color online) The change in optical transmittance of a solid state switching device during cyclic voltammetry at different scan rates of (a) 0.1 V/s, (b) 0.5 V/s, and (c) 0.75 V/s.

current-potential measurements. The cyclic voltammograms of the device are initially checked with lower starting positive and ending negative potentials. However, these lower ranges of potential values are insufficient to recover the absorbed hydrogen and transmittance of the device. After a few trials, it is found that the recovered transmittance of the device satisfactorily reaches its initial value at about 3.5 V with the much slower scanning rate of 1 mV/s. Figures 6(a)–6(c) represent the cyclic voltammograms for the fourth, fifth, and sixth trials, respectively, at different scan rates from 3.5 V toward more negative values up to -2.5 V along with a device transmitting light at 630 nm. In Fig. 6(a), the cyclic voltammogram of the device scanned at 0.1 V/s shows cathodic current starting to rise at about -0.3 V, and a single hydride formation peak is found with its maximum at -1.4 V. The transmitted light of the device starts increasing from 12% at about -0.8 V and reaches its maximum value of 48% at the potential of -1.4 V, where the reduction current starts to decrease again, i.e., the hydride formation process has been completed. The scan is reversed at -2.5 V and in the voltammogram, in contrast to the hydride formation reaction. Two separate stages can be distinguished in the oxidation process. Even though the current peak is observed in the reverse scan at -0.7 V, the transmittance of the device remains constant. Thus it is attributed to oxidation of hydrogen adsorbed at the Pd surface or desorption of absorbed hydrogen from the Pd overlayer.⁸ The increase in the current at 1.7 V results a decrease in transmission due to the hydro-

gen desorption from HMC-H_y film. This process is rather slow compared to the appearance of the transmitting state. Thus the onset of the return to the metallic state is a somewhat slower process than hydrogen uptake. At the potential limit of the scan (3.5 V), the film has not yet come to the initial transmittance state. However, it can be seen clearly in Fig. 6(a) that even at 3.5 V, much anodic current is still developing, which indicates that the discharging process is still not completed; therefore, the recovered transmittance has not reached its initial level. Figures 6(b) and 6(c) show the cyclic voltammogram and change in transmittance of the device at immediate subsequent cycles (fourth and fifth) scanned with scan rates of 0.5 and 0.75 V/s, respectively. In this the value of the initial level of transmission is the same as the recovered transmission in the previous voltammogram. It is observed that there is a definite time lag between the voltammogram and the change in transmission at higher potential scanning rates, where the transmittance starts increasing at much more negative potentials during hydride formation and the transmittance remains in its maximum level during a reverse scan. However, at lower scan rates, this effect vanishes. Since the transmittance for subsequent fourth, fifth, and sixth cycles given in Fig. 4 and the inset of Fig. 5 shows almost the same transmittance levels for both the hydrating and dehydrating states, the observed device percent transmittance change in the charging and discharging states during cyclic voltammetry is assumed to depend mainly on the electrode potential scanning rates. Further, the switching characteristics of the same film have been checked in a KOH liquid electrolyte during electrochemical hydrogenation and dehydrogenation. It was found that the switching properties are largely dependent on the applied electrode voltage and scanning rates of voltage.²⁷ It was also reported recently that the optical switching property of the device largely depends on applied voltages. The switching speed from the reflective state to the transparent and vice versa became faster with an increase in applied voltage. However, the level of the transmittance is the same for all voltages above the critical voltage.¹⁶ The cyclic voltammograms (Fig. 6) show that the transparent state once created at low potentials remains relatively stable up to much higher potentials indicating that the hydride state is in a very stable state.

IV. CONCLUSION

The simple optical switching solid state device (10 × 10 mm²) based on a RCo₂-type alloy hydride thin film with a solvated polymer Nafion® 117 membrane as a solid electrolyte has been developed. The reversible optical switching properties are highly dependent on the applied electrode currents/voltages. The durability of the switching device is limited by the solvated Nafion membrane; however, we believe that an appropriate solvent with higher viscosity and low volatility in the Nafion membrane and proper thick-

ness of the Nafion would prevent the early drop in transmittance of the device and improve switching durability. The main advantage of the device is that it can switch reversibly from a reflective state to a transparent one with a small applied current/potential.

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