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Electrochemical Energy Storage of Silver And Silver Oxide Thin Films in an Aqueous NaCl Electrolyte.

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Abstract:

We present an investigation into the pseudo-capacitive energy storage potential of silver (Ag) and silver oxide (Ag_2O) thin film electrode materials prepared by reactive magnetron sputtering. The growth mode and morphology of the prepared films were investigated using the scanning electron microscope (SEM), which reveals columnar growth structure and microporous sites.

The stoichiometry and oxidation states of the silver oxide films were monitored with X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infra-red spectroscopy (FTIR). The XRD results reveal the nano-crystalline nature of the silver and silver oxide thin films with peak intensities indexed at (111) planes.

Static and dynamic Contact angle measurements were used to probe the penetration of the aqueous NaCl electrolyte into the pores in the prepared silver and silver oxide films, with surface wettability of all (Ag) and (Ag_2O) thin films hydrophilic in nature, which is vital for a good electrochemical performance.

The Faradaic redox reactions, capacitance and the charge discharge of the films when exposed to the NaCl electrolyte, were monitored with cyclic voltammetry and chronopotentiometry charge-discharge. Results show that Silver and silver oxide

possess specific capacitance of 240.52Fg^{-1} and 275.50Fg^{-1} at 2mVs^{-1} respectively, which is promising for electrochemical energy storage application.

Keywords: Silver oxide, surface characterization, wettability, charge-discharge, cyclic voltammetry, pseudocapacitor

1. INTRODUCTION

Global warming has been an issue for decades. Effort has been made by academia, industrial and governmental agencies to solve this problem, by implementing efficient ways of storing energy. Battery systems have helped for a while in doing this, however, it does not suit applications that require fast charge/discharge time and zero percent oxide emission. Ideally, one device that can fill in the gap left by batteries and other storage devices is a Supercapacitor. Supercapacitors offer cleaner, more efficient and a faster charge/discharge time for all round applications like electric and hybrid vehicles [1], mobile phones, digital cameras, electric tools, uninterruptible power supplies, digital communication devices, off-grid solar energy and regenerative braking [2]. Supercapacitors store energy by using either charge separation in a Helmholtz double layer (electrochemical double layer capacitor EDLC) [3] or by fast surface redox reactions (pseudocapacitor) [2]. Different materials have been used over the years to process supercapacitors such as carbon, polymers, with carbon based materials being the predominant one, due to their high cycle stability, high specific capacitance, availability and ease of processing. They have a major downside of inability to withstand high temperature application, low specific energy density and limited cell voltage [4]. These problems can be solved by deploying metal oxide based

electrodes [5] namely ruthenium oxide (RuO_2) [6], cobalt oxide (Co_3O_4) [7], nickel oxide (NiO) [8], Indium oxide (In_2O_3) [9]. Ruthenium oxide been the most performing amongst the transition metal oxide materials for pseudocapacitor application, due to their excellent reversible redox reaction, good thermal stability and broad potential window, with a specific capacitance of 1099Fg^{-1} reported by Pengfei et al. [10]. The high cost of ruthenium oxide and the low conductivity of other metal oxide materials hinder their wider application. Therefore the need to source for other electrode materials that are cheap and exhibits pseudocapacitance close to ruthenium oxide is paramount. Alternatively, radio frequency magnetron sputtered (RF) silver and silver oxide nano-structure electrodes have been proposed, for supercapacitor application. Studies from Patil et al. and Kalambate et al. [11-12], show that composite silver thin films have been used for supercapacitor applications due to their reasonable surface area and good conductivity. Mojtaba et al. [13] conducted a preliminary investigation on the morphology and wettability of silver oxide thin film electrodes and found that silver oxide has porous morphology and reasonable wettability. The performance of supercapacitor is based on reasonable surface area, porosity and wettability, which are in agreement with findings from Patil et al., Kalambate et al. and Mojtaba et al. [11-13]. This makes silver and silver oxide thin films a good candidate for supercapacitor application. The use of nano-structured silver and silver oxide thin film electrodes, combined with the use of aqueous NaCl electrolyte will have a definite impact on the development of high voltage electrochemical supercapacitors and optimise their energy storage and power capability. Such investigation is therefore timely because of the current interest in high performance supercapacitors.

2. EXPERIMENTAL INVESTIGATION

Silver/Silver oxide thin films were deposited by the radio frequency magnetron sputtering method, on microscope glass slide with dimension (25.4mm*76.2mm), and on 304L stainless steel. A Solid silver target was used as the starting material with high purity argon and oxygen gases as the sputtering and reactive gases. The deposition parameters are as shown in Table 1. Prior to the deposition of silver and silver oxide on the glass and 304 stainless steel substrates, the microscopic glass slide and stainless steel were cleaned with isopropanol and then with deionized water in an ultrasonic bath machine to remove any impurities on the surface.

Table 1: Deposition conditions for Silver and Silver oxide thin films on glass and 304 stainless steel.

Forward power (W)	250, 300, 350
Oxygen flow rate (sccm)	10
Argon flow rate (sccm)	60
Reflective power (W)	< 1
Temperature	Ambient
Deposition time (mins)	20

The above deposition conditions yield better stoichiometry, morphology, film stability and controllable surface area. A Siemens d5000 x-ray diffractometer model was used

to characterize the silver and silver oxide thin film stoichiometry and S-4100 scanning electron microscopy (SEM) was used to study the morphology of the prepared Ag and Ag₂O thin films at 250W, 300W and 350W deposition power for better morphology control. Further chemical composition of the prepared silver oxide thin films were analyzed using Nicolet iS50 FTIR equipment and Scienta ESCA 300 spectrophotometer, equipped with a monochromatic Al K α (1486.6 eV) x-ray source, for X-ray photoelectron spectroscopy (XPS). Static contact angle, dynamic contact angle (advancing and receding) and contact angle hysteresis measurements were carried out using the CAM 200 goniometer and KSV sigma 700 Tensiometer. The cycle life and capacitive behavior of silver/silver oxide thin film were studied in a 0.5M NaCl solution using a PGZ 301 Potentiostat. The PGZ 301 Potentiostat comprises a saturated calomel electrode (SCE), platinum wire and the sample surface, acting as the reference, auxiliary and the working electrodes respectively. The charge discharge and capacitance analysis were investigated using chronopotentiometry charge-discharge and cyclic voltammetry for voltage range of -1000 to 700mV at 2mV/s scan rate for better ion diffusion.

3. RESULTS AND DISCUSSION.

3.1 Structural Studies

The XRD pattern of the three silver thin films prepared at 250W, 300W and 350W using RF magnetron sputtering, are as shown in Figure 1(a), with diffraction peaks indexed at (111) and (200) crystal planes, confirming the nano-crystalline nature of the silver (Ag) thin films deposited at various sputtering powers. These peaks are centered at 38.2° and 44.48°, with a face centered cubic structure (FCC), an

attribute of silver thin films without any contamination [14-17]. Moreover, while sputtering power increases, the (111) peak intensity becomes stronger as shown in Figure 1(a). This implies an increase in crystallinity and grain size, with (111) plane having the lowest surface energy [13, 15, 18]. The grain size of the silver film is an important indicator of the crystallization quality, which was calculated using the Scherrer formula.

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \dots\dots\dots(1)$$

Where D is the average grain size, λ is the wavelength of the incident X-ray (for Cu $K\alpha$, $\lambda = 0.154056\text{nm}$), β and θ are the full width at half maximum of the intensity and Bragg angle respectively. Lorentz method was used to analyse the full width at half maximum via magic plot software and Siemens d5000 X-ray diffractometer Eva software. Silver thin films yielded grain size of 27.52nm, 30.12 nm and 32.88nm for Ag deposited at 250W, 300W and 350W respectively similar to Todorov et al. report [15]. The increase in grain sizes with sputtering power signify increase in crystallinity of the silver thin films [15].

1 (a) Ag XRD at 250, 300W and 350W

1(b) Ag_2O XRD at 250, 300W1(c) FTIR of Ag_2O at 250, 300 and 350W**Figure 1.** Shows the XRD and FTIR spectra of thin films Ag and Ag_2O

However, silver oxide thin films deposited at 250W, 300W and 350W reveal similar trend to the Ag films, with a strong X-ray diffraction peaks at 32.7° and 38.2° as shown in Figure 2(b). These peaks at (111) and (002) planes reflect the cubic structure of silver oxide. There is a progressive increase in the intensity and crystallinity of the silver oxide thin films from 250W to 350W, which were calculated using the Scherrer formula. The silver oxide thin films yielded a grain size of 15.15nm, 17.04nm and 20.61nm as the sputtering power increased from 250W to 350W. This indicates

increase in crystallinity of the silver oxide thin films due to the increase in the rate of oxygen diffusion into the silver oxide thin film deposited at 350W compared to silver oxide thin film deposited at 300W and 250W, resulting in larger grain sizes for silver oxide deposited at 350W [13,19-23]. This is in agreement with the scanning electron microscopy images, where there are more pronounced micropores on silver oxide films sputtered at higher forward power. This finding is very vital for engineering silver oxide based materials, for pseudocapacitor applications.

3.2 FTIR

The FTIR result of silver oxide samples prepared at 250W, 300W and 350W is shown in Figure 1(c), the absorption peaks on the 250W, 300W, and 350W at 1105cm^{-1} may be attributed to O-H bending vibrations combined with the silver atoms. The absorption band on 530cm^{-1} is due to Ag-O stretching mode, which corresponds to Ag-O vibration in Ag_2O [24-26]. FTIR finding indicates the dominance of silver oxide Ag_2O in the prepared films, which are in agreement with the XRD results in Figure 1(b).

3.3 XPS

XPS was employed to investigate the chemical state of the deposited thin films. Figure 2 (a and b) shows the Ag 3d and O 1s spectra, with binding energy observed at 368.3eV consistent with Ag sample [19, 27-30]. The existence of Ag-O bond was also evident in the O 1s spectra, with peak at 531.8 eV [19, 31-32]. The 531.8 eV peak originates from the subsurface formation of oxygen, which is a mixture of oxygen and the hydroxyl group. These binding energies are in accordance to standard silver and oxygen binding energies and they support the XRD and FTIR analysis.

Figure 2. XPS and cross- sectional view of Ag and Ag₂O thin films morphology

3.4 Morphological Study

The SEM image in Figure 2 (c) shows a mixture of layer by layer and Volmer-Weber growth mode on silver thin film, while Figure 2(d) shows columnar and porous islands growth mode on the deposited silver oxide thin film. These porous morphologies on the silver oxide thin film facilitate the diffusion of the electrolytes, improves the conductivity, reduces electrodes resistance and accelerates Faradaic

surface reaction, which are very important for supercapacitor application [33-35]. Wei et al., Staiti et al., Zhang et al. and Keraudy et al. [36-39] reported scanning electron microscopy findings that are similar. The pores on the Ag_2O thin films increases with power as shown in Figure 3 (d, e, f), which Sun et al. and Min et al. [40-41] reported as due to an increase in the diffusion rate of oxygen molecules, with a high possibility to assemble greater pores at a higher deposition power. The pronounced nano pores on Ag_2O paves the way for better ions interactions with the electrode/electrolyte interface compared to Ag thin films in Figure 3 (a, b, c). The nano pores are very significant for

Figure 3. Top view of Ag and Ag_2O thin Films SEM Images

Faradaic surface reaction [42].

3.5 Wettability Test

Wettability studies were carried out to investigate the interaction of the silver and silver oxide electrodes with electrolytes, which reveal either the hydrophobic or the hydrophilic nature of silver and silver oxide samples [13]. Contact angle measurement gives access to wettability studies, by using sessile drop techniques (static contact angle) on homogeneous surfaces. Static contact angle measurement is governed by young modulus equation shown in equation (2) [43].

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad \dots\dots\dots (2)$$

where θ , γ_{sv} , γ_{lv} and γ_{sl} represent the contact angle, surface energy of the solid, free energy of the liquid and surface energy of the solid-liquid interface, considered as the thermodynamic interfacial energy parameters for solid-vapor, liquid-vapor and solid-liquid respectively. If the wettability is high, contact angle (θ), will be small and the surface is hydrophilic. On the other hand, if the wettability is low, contact angle (θ) is high indicating the surface is hydrophobic. Figure 4 (a and b) shows the static contact angle plot of Ag and Ag₂O thin films, using KSV Cam 200 goniometer, where water and ethylene glycol are the polar components and diiodomethane the non-polar.

In this present work, the contact angles of the three probing liquid, on the surface of silver and silver oxide thin films are all small ($<90^\circ$), indicating Ag and Ag₂O are hydrophilic in nature [13]. Xingxun et al. proposed that static contact angle tends to decrease as the pore size increases [44], and this stands true with the results obtained

in this research, where the silver oxide thin film deposited at 350W has the smallest contact angle followed by 300W and finally 250W due to well pronounced pores, which are evident on the SEM micrograph as shown in Figure 3 (d, e, f). The hydrophilic property of the silver and silver oxide thin films is an essential factor for a supercapacitor application, with microspores fundamental to better performance [45-46].

4(a) Ag static contact angle

4 (b) Ag₂O static contact angle

4(c) Ag dynamic contact angle

4 (d) Ag₂O dynamic contact angle

Figure 4. Ag and Ag₂O static and dynamic contact angle at deposition power (250W to

Dynamic tensiometry (KSV sigma 700 tensiometer) measures the changes in the net force on the silver and silver oxide thin film surface during the repeated immersion and emersion into the probing liquids, revealing the wetting properties of the silver and silver oxide prepared films at different sputtering power. Most practical surfaces are non-ideal (heterogeneous in nature) and the measurable contact angle in this situation is referred to apparent contact angle, where the contact angle values fall into more or less wide interval between the advancing and receding angles. Factors contributing to these non-ideality are surface immobility and roughness, which are governed by two main theories Wenzel equation (3) and Cassie-Baxter equation (4) [43, 47-48].

$$\cos \theta^* = r \cos \theta \dots\dots\dots (3)$$

Where r is the roughness factor and θ^* is the contact angle on a smooth surface of the same material and θ is the absolute contact angle on the heterogenous surface

Cassie-Baxter developed a technique to calculate contact angle on heterogeneous material and on porous materials as shown in equation (4)

$$\cos \theta^* = f_1 \cos \theta_Y - f_2 \dots\dots\dots (4)$$

Where θ^* = apparent contact angle, θ_Y = equilibrium contact angle and f_1, f_2 are the area fractions of the wetted materials. Figure 4(c and d) show the dynamic contact angle measurement of silver and silver oxide thin films from KSV sigma 700 tensiometer

equipment. The advancing contact angle and the receding contact angles are all less than 90° (hydrophilicity), with the advancing contact angles on silver and silver oxide thin films similar to the static contact angle in Figure 4(a and b). Sara et al. [49] proposes that the roughness and micro pores make the receding angle to be smaller which is noticeable in both silver and silver oxide thin films deposited at various sputtering power. The differences in advancing and receding contact angle are smaller in silver oxide thin films compared to silver thin films, giving rise to smaller contact angle hysteresis. This demonstrates better wettability and penetration of the three probing liquids into the pores/columnar structure of the silver oxide thin films microstructure compared to silver thin films [50-51]. Silver oxide thin films deposited at higher forward power, offered excellent electrolyte penetration/interaction, due to the well-pronounced columnar and porous network structure as shown the SEM micrograph in Figure 3 (d, e, and f).

3.6 Electrochemical impedance spectroscopy (EIS)

The EIS spectra of silver and silver oxide thin films exposed to the saline solution at alternating sine wave amplitude of 10mV, for the frequency range of 100mHz to 10KHz is presented in Figure 5 (a and b) using Nyquist plot. It is evident from the Nyquist plot in Figure 5, that silver and silver oxide thin films deposited at 250W, 300W and 350W, show capacitive behaviour in the frequency range of 100mHz and acts as a resistor at high frequency of 10KHz. Yuksel et al. [52], reported that the absence of semicircle on the Nyquist plot of silver and silver oxide thin film is due to the high conductivity of the silver and silver oxide thin films in high frequency region. The Nyquist plot displays intercalation process, namely ion diffusion in the silver

oxide thin film electrode (Ag_2O 350W), symbolized by the 45° spectra line to the Z_i axis. This is a representation of electrode/electrolyte interface interaction and capacitive behaviour of the deposited silver oxide thin films [53-54]. Braam et al. [55], attributes the 45° spectra line to the Z_i axis to the Warburg impedance diffusion of the hydroxide ion and oxidized species. There is an obvious deviation of silver thin films deposited at 250W, 300W and 350W as shown in Figure 5a from the 45° spectra line to the Z' axis. These deviations, Criado et al. [56] associates to non-homogeneity of the silver thin films coating and the reflective boundary condition at the electrode. Furthermore, Z-view software was used to fit the equivalent circuit model of the silver and silver oxide thin films in saline solution. This gives an indication of the solution resistance (R_s) and polarization resistance (R_p). The equivalent circuit model yielded (R_p) of 21Ω , 9Ω , 6Ω for silver thin films sputtered at 250W, 300W, 350W and 10Ω , 8Ω and 4Ω for silver oxide thin films prepared at 250W, 300W and 350W respectively. Silver oxide thin film deposited at 350W 10sccm, show smallest real impedance, an indication that more energy is stored on silver oxide thin film sputtered at 350W 10sccm.

5 (a) Nyquist plot of Ag thin films

5 (b) Nyquist plot of Ag_2O thin films**Figure 5: EIS spectra of Ag and Ag_2O thin films using Nyquist plot**

3.7 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) curves provide the avenue for evaluating the capacitance of a supercapacitor. CV curves show two different regions, anodic (positive current values) and cathodic (negative current values) where the redox reactions occur respectively. Several important parameters characterize cyclic voltammetry, such as peak currents and peak potentials [57]. Yin et al. [58] stated that the specific

capacitance from the voltammetry curve can be evaluated using the following equation

$$C_s = \frac{I}{mv(V_a - V_c)} \int_{V_a}^{V_c} I(V) dV \quad \dots\dots\dots (5)$$

Where C_s is the specific capacitance in F/g, m indicates the mass of the active electrode material, I the responses current, v is the scan rate and ΔV is the potential range for anodic (V_a) and cathodic voltages (V_c). The supercapacitive performance of silver thin films prepared at different deposition powers of 250W, 300W and 350W were characterized using cyclic voltammetric techniques. Figure 6 shows the three silver thin film electrodes CV, with redox peaks both on the anodic and cathodic sides, due to faradaic reactions. This implies that the capacitance associated with silver thin films electrodes are pseudocapacitive in nature. Dar et al. [59] reported that the peaks at the cathodic and anodic sides of the CV are due to the diffusion, interfacial kinetics reaction and ion transfers at efficient rates, meaning anions are exchanged between the electrode and electrolytes during redox reaction as shown in equation (6 and 7) [59-61]. The CV of silver thin films deposited at different sputtering power observed in Figure 6 are similar to the ones observed by [62-63], with the oxidation peak of the three silver thin films located at +0.4V. The appearance of peaks at the anodic side of Ag thin films is due to the oxidation of Ag in the presence of the Chloride ion [64-65] as shown in equation (6),

A reverse process is seen at the cathodic side of the silver thin films of 250, 300 and 350W with peaks located at -0.5V, due to the reduction of Ag₂O to Ag [64].

Figure 6. Cyclic voltammetry (CV) of Ag thin films.

The CV of silver oxide thin films deposited at different forward power at oxygen flow rate of 10sccm are as shown in Figure 7, with anodic peaks located at +0.4V for all the

samples of silver oxide thin films [62-63]. The appearance of peaks at the anodic side of Ag₂O thin film is due to the oxidation of Ag₂O in the presence of the Chloride ion [64] as shown in equation (8), with the anodic current observed, which Zhang et al. [62] attributed to chemisorption process, rapid oxide nucleation and ion migration into the microspores revealed in the SEM analysis [65].

A reverse process is seen at the cathodic side of the silver oxide thin films deposited at 250, 300 and 350W at 10sccm oxygen with peaks located at -0.5V, due to the reduction of Ag₂O [64-65].

The specific capacitance of silver oxide thin films deposited at 250W, 300W and 350W were calculated using equation (5) and results shown in table 2. Peak current at each of the voltage levels of the anodic and cathodic sides of the silver and silver oxide thin films, indicate pseudocapacitance behaviour. This symbolise effective utilization of active electrode material by electrolyte ions during electrochemical reaction. More specific capacitance is generated by silver oxide thin films deposited at 350W, 300W, and 250W compared to silver thin at 350W, 300W, 250W as shown in table 2, due to the formation of well-interconnected pores, which pave the way for better penetration and interaction of the silver oxide thin film electrodes with the electrolyte, yielding better electrochemical performance [65]. The higher capacitance values obtained for silver oxide thin films electrode is attributed to presence of more

pronounced pores, columnar growth structure, which makes way for better electrolyte penetration.

Figure 7. Cyclic voltammetry (CV) of Ag₂O thin films.

The specific capacitance of the three silver thin films were calculated using equation (5), with specific capacitance decreasing with sputtering power. This is ascribed to

better wettability and diffusion of ions at higher sputtering power, inline with the SEM micrograph and contact angle measurement.

Table 2. Specific Capacitance of Silver and Silver Oxides at different Sputtering Powers

Sample/ Scan rate (2mV/s)	Deposition Power (W)	Specific capacitance (F/g)
Ag	250	207.45
Ag	300	230.68
Ag	350	240.52
Ag ₂ O	250	210.21
Ag ₂ O	300	232.34
Ag ₂ O	350	275.50

To further get more information on the electrochemical stability of the sputtered silver and silver oxide thin films, charge-discharge cycling test was carried out at current density of 1Ag^{-1} for ten thousand cycles as shown in Figure 8. The specific capacitance retention of silver and silver oxide thins decreased after 7800 cycles to around 7%. This gives rise to specific capacitance retention of 93%, an indication of a reasonable cyclic stability of silver and silver oxide thin films [52-53].

8 (a) Ag thin films

8 (b) Ag₂O thin films

Figure 8. Capacitance cyclic test of Ag and Ag₂O thin films

3.8 Charge -discharge

The capacitive behaviour of silver and silver oxide thin films were examined by chronopotentiometry charge-discharge for voltage range of -1000 to 700mV as shown in Figure 8 and 9. The pseudocapacitance of the deposited silver and silver oxide thin films were calculated using equation (10).

$$C = \frac{I}{m(dE/dt)} \dots\dots\dots (10)$$

Where $[(dE/dt)]$ is the slope of the charge discharge curves, m mass of the Ag and Ag_2O thin films, I = current, C is the specific capacitance in F/g

The charge-discharge curves in Figure 9 for the silver thin films prepared at 250W, 300W and 350W appear to be symmetrical, which is an indication that the capacitance behaviour is due to faradaic reaction. This is in agreement with the results obtained for silver CV measurements shown in Figure 6, which reveals redox peaks, as a result of the oxidation (charging curve) and reduction (dis-charge curve) reaction at the interface of the silver thin film electrodes and the electrolytes as shown in equation (6) and (7). Berchman et.al [66] proposed that the sudden rise in the charging cycle voltage of the three silver thin film electrodes is due to the electrolysis of water. Using equation (10), the specific capacitance of silver thin film electrodes were calculated, yielding Specific capacitance of 150.25, 170.12 and 200.41F/g for silver films prepared at sputtering power of 250W, 300W and 350W. The decrease in specific capacitance as sputtering power decreased is due to the less migration of ions to the active areas of the thin film silver electrodes materials, resulting in lower charge storage and hence a low specific capacitance [67-68]. This is inline with the contact angle and morphological analysis, where silver thin film electrodes prepared at higher power, has better wettability and pronounced pores in the microstructural arrangement. Furthermore, the charge-discharge curves of the silver oxide thin films in Figure 10, prepared at 250W, 300W and 350W appear to be mirror images of each other, which confirms that the capacitance behaviour is mainly due to faradaic reaction. This is in agreement with the silver oxide CV in Figure 7 which reveals redox peaks, as a result of the oxidation (charging curve) and reduction (dis-charge

curve) reaction, at the interface of the three silver oxide thin film electrodes and the electrolytes, as shown in equation (8) and (9). Charge storage is due to the surface adsorption of cations and the intercalation/de-intercalation of ions into the silver oxide thin film electrodes, during oxidation and reduction cycle, which Radhamani et.al proposed [69]. Using equation (10), the specific capacitance of silver oxide thin film electrodes were calculated, resulting in Specific capacitance of 168.02, 200.10 and 235.01F/g for silver oxide film prepared at deposition power of 250W, 300W and 350W. Morphology and wettability been some of the key parameters for a supercapacitor to retain higher specific capacitance. Silver oxide thin film prepared at 350W demonstrated this, giving lower contact angle and well pronounced columnar growth structure, leading to better ion migration, diffusion and higher specific capacitance, compared to the rest of thin films prepared at different deposition power [64, 69-70].

9 (a) Ag at 350W

9 (b) Ag at 300W

9 (c) Ag at 250W

Figure 9. Charge-discharge of Ag thin films.

10 (a) Ag_2O at 350W 10 (b) Ag_2O at 300W 10 (c) Ag_2O at 250W**Figure 10. Charge-discharge of Ag_2O thin films.**

CONCLUSIONS:

Radio frequency sputtering techniques have been used to produce suitable and columnar microstructure silver and silver oxide thin films for pseudocapacitor application. The electrolyte penetration was supported by combining goniometer and tensiometer analysis, which revealed the hydrophilic nature of silver and silver oxide thin films, with smaller receding contact angle values, indicating electrolyte wetting/penetration into the thin films. The contact angles decreased with increase in pore structure and sputtering power, with tensiometry providing the relationship between the advancing, receding, contact hysteresis and wettability.

Furthermore, results from cyclic voltammetry reveal that silver oxide thin film possess a specific capacitance of 275.50F/g at 2mV/s compared to 240.52F/g at 2mV/s for silver thin film. This makes silver oxide a viable electrode material for supercapacitor application.

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HIGHLIGHTS

- Surface wettability of prepared Ag and Ag₂O thin films are hydrophilic in nature.
- Tensiometer analysis reveal electrolyte penetration and contact angle hysteresis.
- Ag and Ag₂O Microstructure are deposition power dependent.
- CV results showed compact anodic and cathodic peaks with 275.50F/g capacitance.