Power Saving Electrochemical Processing of Low Cost MnO$_2$@Porous Al Electrode for High Performance Supercapacitors Applications

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Abstract:

The supercapacitive properties for MnO$_2$ coated on porous aluminum foil Al electrodes etched using various acidic baths and ethylene glycol (EG) as additive was studied. The optimum current densities for achieving high porous surface of Al foils using galvanostatic technique are 70 and 90 mA/cm$^2$ in case of etching from acidic solution and when ethylene glycol is added respectively. Furthermore, cyclic voltammetry, galvanostatic charge–discharge techniques and electrochemical impedance spectroscopy were performed to determine specific capacitance and cycle life of the MnO$_2$@ porous Al foil and MnO$_2$@porous Al-EG electrode using 0.5 M Na$_2$SO$_4$ as electrolyte. The cyclic voltammetric curves for the two electrodes reveal that pseudocapacitive behavior during oxidation–reduction reaction with maximum specific capacity 221.5 F/g at scan rate 20 mV/s for MnO$_2$@ porous Al electrode. Moreover, the galvanostatic charge–discharge tests for MnO$_2$@porous Al electrode at current densities 0.5 and 1 A/g show good pseudocapacitive performance and cycle ability with nearly linear curves forming quite triangle shape. Also, The EIS curves for both electrodes elucidate that, the total impedance of MnO$_2$@porous Al cell is smaller than that of MnO$_2$@porous Al-EG cell, so, MnO$_2$@porous Al electrode has a high ionic conductivity between active material and ionic species. In addition to, both electrodes posses quite similar capacitive retention about 75% after 1000 cycles and this reveals the good adhesion and less dissolution of MnO$_2$ film.

1. Introduction:

Recently, alternative energy resources and environmental pollution are the most important world concerns [1, 2]. In addition, the increasing demand for energy materials and improving the high-performance energy-storage devices has gained much attention [3]. Therefore, the fabrication of electrode materials has become an important research
field to fabricate long cycle life, low cost, light weight and productive energy storage apparatus [3, 4]. The usage of these materials is found in various applications like solar cells [5], fuel cells [6], lithium battery [7] and supercapacitors [8] with excellent energy density and power density. Although the batteries have shared the major role in the energy storage systems for various applications ranging from wristwatches to cars and more recently electrical grid. Since, the low life cycle, low power density and high cost of energy are still the main drawbacks for batteries [8, 9]. As a result, supercapacitors are emerged as new energy storage technology in comparison to batteries due to their ability to store and release energy instantaneously, long life, lower cost and high power density. They have many applications as uses in electric vehicles, consumer electronics, portable devices and wherever a burst of energy supply is needed [2, 9, 10]. Electrochemical capacitors are commonly referred as supercapacitors, therefore, the storage mechanism of supercapacitors can be classified as electrochemical double layer capacitors (EDLCs) or non-faradic supercapacitors, while the other one is faradaic pseudocapacitors or redox supercapacitors and Hybrid supercapacitors [2, 11-15]. In hybrid SCs, both the EDLC effect and the pseudocapacitance can be simultaneously generated in a single SC. The hybrid SC one can achieve higher energy and power densities with good cycling stability by collecting Faradaic and non-Faradaic processes to store the charges.

Ruthenium oxide (RuO₂) is supposed as one of the most promising pseudocapacitors exhibiting a specific high capacitance 720 F/g [16]. However, RuO₂ is expensive and toxic which has limited its commercial viability in supercapacitors. Great efforts have been done to enhance alternative cost-effective transition metal based electroactive materials, especially, earth-abundant transition metal elements in Period 4, 5 and 6 of the periodic table as Ni, Co, Mn, Cd, Fe, Mo, W, V and Ti, have been used to design electroactive materials because of their multivalent states [10, 17]. Obviously, some of transition metal oxides, such as Co₃O₄, NiO TiO₂, and MnO₂, also have pseudocapacitance. Manganese dioxides MnO₂ has become hotspot in recent research for its abundant resource, toxicity, wide voltage range [2, 18, 19] and good electrochemistry performance [20, 21]. Besides, the equivalent series resistance (ESR)
for current collectors is considered as indicators affecting on the performances of super capacitors. The presence of the ESR in current collector has led to the reduced charge range and weakened storage capacity. Therefore, the low resistance, high conductivity, and low cost of the aluminum foils make it the acceptable choice as current collector materials, thus the etching process of the aluminum foils will greatly affect the overall performance of the supercapacitor [22]. There are three methods for etching of Aluminum foil, physical method, chemical etching, and electrochemical etching. Nowadays, the electrochemical etching is developed on the basis of chemical etching, by increasing the electric field, and fastens the process of aluminum foil etching. Therefore, the applied electric current density is proportional to the dissolution rate of aluminum foil, hence, the density of impressed current could be adjusted to control the speed of aluminum foil etching [22]. Plainly, the electro etching of Al disk was carried out using galvanostatic technique which is a simple one, easy to handle, economic and friendly environment [23, 24].

In this regard, the goal of this work is to study the anodic etching of aluminum disk using aqueous medium and ethylene glycol medium to create highly porous low cost current collector. Furthermore, the electrochemical performance of the etched Al disk as current collectors for asymmetric MnO₂ supercapacitors will be systematically envisaged. Finally, the capacitance and cycle life of the MnO₂ coating layers will be compared for the different porous Al disks anodically etched by various electrolyte systems.

2. Experimental:

2.1. Electroetching of Al disks

The highly pure Aluminum (Al disk) was etc hed using Galvanostatic technique to form porous Al disk. This job was done via studying various current densities ranging from (50 to 120 mA/cm²), etching times (from 5 min to 20 min), and different electrolyte mediums. The inorganic mediums are mixture of 3 M HCl+ 1 M H₂SO₄, 3 M HCl+ 1 M H₃PO₄. Also, the organic acids as citric and acetic acid were used with the same ratio with 3 M HCl. Moreover, the effect of ethylene glycol presence as organic material with ratio 1: 4 mixture of HCl+ H₂SO₄ was studied. All of the above experiments were carried
out at room temperature, while most of works related to etching of Al disk were performed at high temperatures (50-70°C) [25]. All of the electrochemical experiments was performed in a standard three-electrode system using Potentiostat (Volta lab 21) at room temperature. A platinum sheet and silver/silver chloride were served as the counter electrode and reference electrode, respectively. While, the working electrodes are Al disks. All of the reported parameters were studied to examine the optimum conditions for getting porous surface of Al disk.

2.2. Electrode fabrication

Pure MnO₂ as active material is mixed with carbon black as conductive material and binder like polyvinylidene difluoride (PVDF) in the ratio of 70:20:10 wt%. Typically, the homo-generous slurry was prepared by mixing all the components in presence of N-methyl pyrrolidone (NMP) as a solvent. Then, the aluminum disk substrates were coated using lab vacuum film coater with the prepared ink followed by drying at 70°C overnight. Then the formed electrodes (working electrodes) are ready for the electrochemical behavior measurements using battery tester.

2.3. Characterization

Cyclic voltammograms were performed with a computer controlled potentiostat (Volta-lab 21), PGP201 potentiostat, a galvanosatat 20V, and a 1A with general generator. The change in the microstructure of the formed of samples was inspected by field emission scanning electron microscopy (JEOL-JSM-5410, Japan). Moreover, lab vacuum film coating machine was used for electrode fabrication with controlled thickness around 1.55 mm. In addition to, the total porosity and pore size distribution were measured by high pressure mercury prosimeter, micrometrics 9320, USA, (30000 psi, motor driven).

2.4. Electrochemical performance measurements

The working electrodes are two types; MnO₂@porous Al disks which produced from HCl/H₂SO₄ bath and MnO₂@porous Al-EG disks which produced using HCl/H₂SO₄/EG as etching bath, while, the platinum sheet was served as counter electrode. The
electrolyte solution was 0.5M Na₂SO₄ solution. Cyclic voltammetry, electrochemical impedance spectroscopy and Galvanostatic charge–discharge techniques were performed using multichannel battery tester Biologic MPG-205, France to study the electrochemical capacitive behavior and cycle life of the as-prepared electrodes. The specific capacitance of the electrode materials can be calculated from the galvanostatic discharge curve according to the following formula [25]:

\[ C = \frac{I\Delta t}{m\Delta V} \]

where the specific capacitance (C) applies to the single electrode (MnO₂ films), I is the discharge current. \( \Delta t \) and t is the discharge time of the asymmetric two electrode cell, respectively. \( \Delta V \) means the voltage window of the asymmetric device, m is the weight of the electroactive material MnO₂ on the porous Al electrode.

### 3. Results & discussions

#### 3.1. Electrochemical processing of porous Al substrate

##### 3.1.1. Effect of current density

The electrochemical etching technique includes the immersion of the Al foil in an aggressive bath to create a pitting corrosion on the surface of aluminum foil which leads to deep channels with a diameter size of few microns [26]. Figure 1 shows the potential – time transients for etching Al foil in an electrolyte solution composed of 3 M HCl:1M H₂SO₄ at various current densities starting from 50 to 120 mA/cm² at room temperature. It is obvious that by increasing the etching current density, the etching potential for the Al foil sharply increases during the first seconds of the anodic polarization which indicates the increasing dissolution of the metal. Then, the potential stabilizes around -0.8 to -1 V in case of 50 and 120 mA/cm² respectively. Chloride ion is counted one of the strongest corrosive anion, thus aluminum foil form a certain shape of corrosion hole because the halogen acid corrosion is considered to be the best medium for aluminum foil etching. The applied current density is proportional to the dissolution rate of aluminum foil. So, increasing current density from 50 to 120 mA/cm² fasten the process of Al foil etching [22, 26]. Figure 2 represents the FESEM images for Al foil anodized at
different current densities from 50 to 120 mA/cm$^2$ for 15 min using 3M HCl and 1 M H$_2$SO$_4$ as electrolyte. It is found that there is no great difference in the morphology of etched Al foil through increasing current density. In addition, EDX analysis confirms that there is no formation for Al$_2$O$_3$ with raising current density from 70 mA/cm$^2$ to 120 mA/cm$^2$ during etching process and only Al metal appears at all motioned current densities as represented in Figure 3. However, the etched Al foil at 90 and 120 mA/cm$^2$ are so brittle and it is difficult to handle. Accordingly, the optimum current density for etching is selected at 70 mA/cm$^2$.

3.1.2. Effect of etching time

Figure 4 (a) reveals the FESEM image for the Al foil in absence of etching solution, while Figures 4 (b, c and d) shows the FESEM for Al foil in presence of etching solution after different etching times ranging from 5 to 15 min at 70 mA/cm$^2$ of current density. It is clear that the aluminum surface shows porous topology as expected, due to the anodic dissolution of the aluminum. Moreover, the nucleation sites are distributed homogeneously among the surface of the foil. The average roughness was found to be around 2.5–2.9 µm. Figure 5 represents the relation between weight losses of Al foil and etching time. It is found that increasing etching time enhances the dissolution of Al foil which causes thinning of Al foil. With rising etching time more than 15 min, the Al foil becomes unstable and so brittle, so it is rubbed off. For this reason, the optimum etching time is 15 min [27, 28]. In contrast to previous trials for Al foil etching using high temperature mediums [26, 27], all the above experiments are carried out at room temperature.
Figure 1. Galvanostatic transients for Al foil etching at various current densities for 15 min at room temperature
Figure 2. FESEM images of Al foil etched using H$_2$SO$_4$ in addition to HCl as electrolyte, etching time 15 min, current density, a) 50 mA/cm$^2$, b) 70 mA/cm$^2$, c) 90 mA/cm$^2$, d) 120 mA/cm$^2$

Figure 3. EDX spectrum for Al foil etched using H$_2$SO$_4$ in addition to HCl as electrolyte, current density a) 50 mA/cm$^2$, b) 70 mA/cm$^2$, c) 90 mA/cm$^2$ for etching time 15 min
Figure 4. FESEM images of Al foil using H$_2$SO$_4$ in addition to HCl as electrolytes, current density 70 mA/cm$^2$, b) 5 min, c) 10 min, d) 15 min. a) blank Al foil without any treatment
Figure 5. The relation between weight loss of Al foil and etching time at current density 70 mA/cm² and at room temperature.

3.1.3. Effect of anions of etching electrolyte

The FESEM images for Al foil surface using various electrolytic etching mediums such as 1 M of citric acid, 1 M oxalic acid, 1 M phosphoric acid and 1 M sulphoric acid in addition to 3 M HCl at 15 min etching time and 70 mA/cm² current density are appeared at Figure 6 (a, c, e, g). It is found that the nucleation sites for etched Al foils using citrate, oxalate and phosphate electrolytes are not uniformly distributed and anodic layer of Al₂O₃ is clearly observed as shown in Figure 6 (a, c & e) [29, 30]. Moreover, EDX analysis spectrum in Figs. 6 (b, d, f & h) revealed the presence of oxygen and phosphorus atoms in case of phosphoric acid. Generally, the oxide layer formation is not favorable, because it inhibits the supercapacitive property for the electroactive MnO₂ coat [29]. Furthermore, the highest weight loss for the different etching electrolytes used is significantly noticed in presence of phosphate and sulphate anions along with the HCl solution as illustrated in Figure 7. On the other hand, the surface of etched Al foil using 3 M HCl and 1 M H₂SO₄ electrolyte in Figure 6 (g) shows a uniformly distributed porous morphology and the absence of oxide layer is clearly evinced ensured via EDX analysis.
as shown in Figure 6 (h). As a result, the optimum electrolyte medium for etching of Al foil in our work is a mixture of HCl and H₂SO₄ at room temperature.
Figure 6. FESEM & EDX spectrum of Al foil using inorganic acids, a, b) citric, c, d) oxalic, e, f) phosphoric, g, h) H$_2$SO$_4$ in addition to HCl as electrolytes, current density 70 mA/cm$^2$, 15 min etching time.
3.1.4. Effect of organic additives

Figure 8. represents the FESEM images for the etched Al foil using ethylene glycol as organic additive in addition to the mixture of 3 M HC+ 1 M H₂SO₄ at various current densities from 50 to 90 mA/cm² for 15 min. as etching time. The ratio of ethylene glycol to the electrolyte mixture is 4:1 [31]. It was reported that the addition of various organic compounds such as ethylene glycol to acidic electrolytic solutions such as H₂SO₄ decreases the ability of porous anodic alumina (PAA) layer in comparison to ethanol as other organic additive [31]. In addition, the organic additives could enhance the rate of arrangement of (PAA) as a result of the gradual decrease in current density. Particularly, it was found that the addition of a miscible organic solvent with small dielectric constant e.g. ethylene glycol (dielectric constant ε= 37 at RT) [32, 33] to aqueous electrolytic solution decreases the rate constant of water which is 80.1 at room temperature [21, 31]. Figures. 8 (a-c) depict the FESEM images for the Al foil etched surfaces in presence of EG as organic additives at various current densities. It noticed
that more uniformity and homogeneity was achieved for the surface after addition of ethylene glycol. With increasing current density from 50 to 90 mA/cm², the morphology of PAA layers appeared as agglomerated layers and the average pore diameter is increased from 2.01 to 2.4 µm.

![Figure 8. FESEM images of Al foil etched using ethylene glycol in addition to mixture of 3 M HCl+ 1 M H₂SO₄ as electrolyte, etching time 15 min, current density, a) 50 mA/cm², b) 70 mA/cm², 90 mA/cm².](image)

3.2. Electrochemical performance of assembled electrodes

3.2.1. Specific capacitance and galvanostatic cycling

In order to evaluate the supercapacitive properties of the MnO₂@porous Al and MnO₂@porous Al-EG electrodes prepared from different etching baths, the cyclic voltammetry tests are performed within potential window 0.0 – 1.0 V at scan rates 20, 40, 60, 80 and 100 mV.s⁻¹.

Figure. 9 (a) reveals the quite rectangular-like shape for the CV curves indicating high similarity in the charge and discharge cycles of the as-prepared MnO₂@porous Al electrode. It is found that the maximum specific capacitance is reached about 221.5 F.g⁻¹ at 20 mV.s⁻¹. In addition, the cyclic voltammetry curves of MnO₂@porous Al-EG electrodes prepared with addition of EG illustrate the similar pseudocapacitive behavior during the oxidation/reduction process as depicted in Figure. 9 (b). Interestingly, the estimated capacitance values are comparable with the reported value using more expensive current collector (porous Ni foam) [34-36]
Remarkably, the calculated specific capacitance values of $\text{MnO}_2@\text{porous Al}$ electrodes are gradually decreased from 221.5 to 132.2 F.g$^{-1}$ with increasing scan rate from 20 mV.s$^{-1}$ to 100 mV.s$^{-1}$, respectively as shown in Figure 9 (c). Eventually, the gradual increase in the area under CV curves is a good confirmation for the direct proportionality between CV currents and scan rates of CV, which demonstrates that, an ideal capacitive behavior. Likely, the specific capacitance of MnO$_2$@porous Al-EG electrodes are slightly decreased from 131.5 to 45 F.g$^{-1}$ with increasing scan rate from 20 mV.s$^{-1}$ to 100 mV.s$^{-1}$, respectively as shown in Figure 9 (c). The noticeable decrease in the specific capacitance values of both type of electrodes suggests that the electrode surfaces did not have the enough exposure time to allow more cations (de-) intercalate to the bulk of the MnO$_2$ active material [37]. Moreover, the galvanostatic charge–discharge tests are performed on $\text{MnO}_2@\text{porous Al electrode}$ in 0.5 M Na$_2$SO$_4$ at two different current density 0.5 and 1 A.g$^{-1}$ as illustrated in Figure 9 (d). The plot indicates good pseudocapacitive performance and cyclability with nearly linear curves forming quite triangle shape [37, 38].
Figure 9. (a) Cyclic voltamograms of MnO$_2$@porous Al electrodes produced by aqueous etching with addition of ethylene glycol at different scan rates of range 20-100 mV.s$^{-1}$, (b) Cyclic voltamograms of MnO$_2$@porous Al-EG electrodes produced by aqueous etching with addition of ethylene glycol at different scan rates of range 20-100 mV.s$^{-1}$, (c) Variation of specific capacitance of MnO$_2$@porous Al electrodes with changing scan rates, (d) Galvanostatic charge-discharge curves of MnO$_2$@porous Al at two different current density 0.5 and 1 A.g$^{-1}$.

3.2.2. EIS studies and cycle life

Figures 10 (a and b) represent the Nyquist plots of both types of electrodes, each plot is commonly composed of at high frequency and a straight line at low frequency. This combination indicates that the electrode process was controlled by electron transport and diffusion of electronic species. Basically, the EIS spectra imply three main
compartments including electrolyte resistance \( (R_s) \), charge transfer resistance \( (R_{ct}) \) and diffusion resistance of electrolytic ions \( (Z_w) \) \[39, 40\]. By comparing the EIS curves for both types of electrodes, it can be noticed that the total impedance of MnO\(_2@\)porous Al cell is smaller than that of MnO\(_2@\)porous Al-EG cell. Meanwhile, the slope of the straight line in the low frequency region confirms the capacitive behavior of the each electrode suggesting excellent capacitive behavior associated to inclination from 45° to 90° in the first cycle. The observed fall in inclination of the straight line after 25\(^{th}\) and 50\(^{th}\) cycles indicates the increase in the values of \( Z_w \) value \[41\].

Figure 10 (c) reveals the cycle life performance of both electrodes over 1000 cycles. It is observed that MnO\(_2@\)porous Al exhibits better cyclic performance as a result of the enhanced ionic conductivity between the active material and ionic species in the electrolyte during cycling. However, both types of electrodes possess quite similar capacitive retention about 75% after 1000 cycles which indicates good adhesion and less dissolution of MnO\(_2\).
Figure 10. (a) Nyquist plots for MnO$_2$@porous Al cell after 1$^{\text{st}}$, 25$^{\text{th}}$ and 50$^{\text{th}}$ cycles at amplitude 10 mV, (b) Nyquist plots for MnO$_2$@porous Al-EG cell after 1$^{\text{st}}$, 25$^{\text{th}}$ and 50$^{\text{th}}$ cycles at amplitude 10 mV, (c) Cycle life performance of the supercapacitive electrodes

Conclusion:

- The supercapacitive properties for the MnO$_2$ @ porous Al and MnO$_2$ @ porous Al-Ethylene Glycol electrodes were studied.
The etching process was carried out using various acidic mediums as citric, oxalic, phosphoric, Sulphic in addition to HCl. Also, ethylene glycol was added as organic additive.

The mixture of 3 M HCl and 1 M H₂SO₄ is the most suitable bath for etching process, due to the absence of aluminum oxide layer and uniform distribution of porous surface as indicated by FESEM and EDX.

Cyclic voltammetric curves for MnO₂ particles coated with screen printing technique on the porous Al foil and at porous Al-EG electrode have pseudo capacitive performance. The maximum specific capacity is recorded at 221.5 F/g at 20 mV/s for MnO₂@porous Al electrode.

The total impedance of MnO₂@porous Al cell is smaller than that of MnO₂@porous Al-EG cell Using EIS data, and both electrodes have similar capacitive retention about 75% after 1000 cycles.

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