Enhanced conductivity of supercapacitor based PAni-GO-Cellulose-Lanthanum using modification of Al current collector surface and gamma irradiation

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Abstract. Conductivity of supercapacitor based PAni-GO-Cellulose-Lanthanum has been improved by modifying the surface of Al current collector using chemical etching methods and gamma irradiation. The purpose of this research is to study the effect of surface roughness of current collector, and radiation dose of gamma irradiation to interface resistance, internal resistance, and conductivity supercapacitor. The roughness of the Al current collector surface can increase the contact area between the electrode and the current collector by increasing the adhesion force, while the irradiation of the PAni-GO-Cellulose-Lanthanum electrode material can improve the wettability properties of the electrode with increasing carboxyl group, thus helping the ion dispersion process in the electrode. The experimental results showed that the chemical etching process at 0.4 N NaNO₃ concentration, and irradiation dose at 40 kGy gave a synergistic effect on the performance improvement of the supercapacitor by decreasing the resistance interface to 109.67 Ω and the internal resistance to 122.63 Ω, also increasing the conductivity to 1160 μS/cm. The improved conductivity properties of the supercapacitor cell represent an alternative promising candidate for the application as energy storage devices and offered a new facile method.

1. Introduction
Today's modern society demands solution to solve energy problem through the development of renewable and zero emission energy, such as wind power, solar power, and hydro power. Applied in many field such as portable electronic device and electric vehicles, energy storage device are required. One of the energy storage devices considered potentially to be developed in the future is supercapacitor, battery, and fuel cell. Supercapacitor is an energy storage device that combines the high energy storage capability (energy density) of batteries with the high power delivery capability of capacitor [1,2]. Supercapacitor is an integrated system, so its performance is not only influenced by one component, but also other constituent components, such as electrode, current collector, and electrolyte [3]. Therefore, modifications to one of the constituent components such as current collectors and electrodes can be an effective approach for realizing high-performance of supercapacitors.

Efforts to improve the performance of supercapacitor are to minimize the voltage lost during the charge and discharge through decreasing the resistance. One source of resistance from the manufacture
of a supercapacitor is the interface distance between Al current collector and the electrode material. Modification of Al surface roughness as current collector can improve the interface contact between current collector and electrode material by increasing adhesion force [3-6]. A functional group on a carbon electrode material may affect the resulting electrochemical properties. The functionality of carboxyl groups on the surface of the graphene oxide derivative through gamma irradiation will improve the hydrophilic properties of the material. Increasing the hydrophilic properties of the electrode material may cause an increase in conductivity due to its excellent wettability to the electrolyte solution. Conversely, excessive carboxyl groups will damage the structure and degrade the performance of the electrode. The balance between hydrophilicity and conductivity is an important key for obtaining an electrode material that provides optimum performance [7-11]. In addition to enhancing the hydrophilic properties, the carboxyl group in the main chain of a compound can increase the conductivity of a material in two ways, namely (i) increasing the flexibility of the chain and (ii) enabling easier movement of the charge along the chain [12-13]. Gamma irradiation is also performed to control the amount and distance of interface layer graphene by controlling the energy. A thin monolayer or few layer structures will reduce the charge transfer distance so as to increase the conductivity and contact surface area that will increase the capacitance [14-15].

Supercapacitor assemblies based on different materials with various methods have previously been studied. To the best of our knowledge, there have been no known studies on a comprehensive effect of chemical etching for Al current collector and gamma irradiation on enhanced conductivity supercapacitor. In the present study, the effects of etching solution concentration and radiation dose on conductivity supercapacitor cell based Polyaniline-Graphene Oxide–Cellulose–Lanthanum (PAni-GO-Cellulose-La) were investigated.

2. Experimental

2.1. Synthesizing of hybrid electrode based PAni-GO-Cellulose-La
Graphene oxide (GO) material is synthesized from graphite powder using the Hummer method [1,16]. The PAni-GO-Cellulose Lanthanum hybrid electrode is prepared by the grafting copolymerization reaction with a gamma irradiation as an initiator. Prior to the grafting process, 3 g GO was dissolved into 50 mL HCl 1 M (Solution A). Solution B is prepared by dissolving 3.6 g of NH4SO3 and 0.5 mL methyl methacrylate into 50 mL HCl 1 M. Then, solution A is added with 12 mL aniline, 1 g La(NO)3.6H2O, and 1 g Cellulose. The mixture is stirred for 1 hour and added solution B while continuously stirring in ice bath until green flocculants is formed. The mixture was then irradiated at a dose of 40 kGy for the grafting process. The result of irradiation was filtered and dried in an oven at 80 °C.

2.2. Surface modification of Al current collector
Modification of Al current collector surface roughness is done by chemical etching method with various concentration of etching solution. Before etching process, Al plate is cut with size 4x4 cm and washed with acetone to remove dust and dirt. Al metal is immersed for 1 minute in an etching solution that consist the mixture of NaOH and NaN3O3 with concentration variations as in Table 1. Then, the Al was rinsed with dilute HNO3 solutions and aquadest. The Al current collector is formed into a circular container with a diameter of 2.5 cm and a height of 2 mm.

2.3. Coating PAni–GO–Cellulose–Lanthanum electrode material on Al current collector
PAni-GO-Cellulose-Lanthanum powder is incorporated into the 5 % PVDF binder. The mixture was stirred with a magnetic stirrer for 30 minutes, followed by ultrasonification for 30 minutes to form homogeneous slurry. The slurry is coated on Al current collectors that have been made and dried at room temperature to form the pouch. The supercapacitor pouchs were assembled using whatman 40 filter paper as separator and H2SO4 1 N as electrolyte solution.
Table 1. Concentrations variation of etching solution

| No | NaOH (N) | NaNO₃ (N) |
|----|----------|-----------|
| 1  | 1.25     | 0         |
| 2  | 1.25     | 0.1       |
| 3  | 1.25     | 0.2       |
| 4  | 1.25     | 0.3       |
| 5  | 1.25     | 0.4       |
| 6  | 1.25     | 0.5       |
| 7  | 1.25     | 0.6       |

2.4. Functionalization of carboxyl groups on the electrodes with gamma irradiation

The slurry mixtures of PAni-GO-Cellulose-La were irradiated with various dose i.e. 0, 20, 40, 60, and 80 kGy. The irradiated slurry is evaporated solvent. The addition of carboxyl groups to the surface of PAni-GO-Cellulose-La electrode due to gamma irradiation was analyzed by Boehm titration method [16].

2.5. Characterization of Supercapacitor

The morphological analysis of Al surface roughness was performed using optical microscope, while the measurement of adhesion force through surface roughness was analyzed by contact angle measurement using Dino Lite portable microscope [17]. Electrical test parameters for characterization of supercapacitor devices include testing of interface resistance, internal resistance, and conductivity using Metrohm Autolab.

3. Result and discussion

3.1. Effect of chemical etching on roughness and contact angle Al

The difference in morphological structure before and after etching was analyzed using optical microscope with 20 times magnification which is shown in Figure 1. In Figure (1b) it is seen that on the surface of Al metals after treatment appear small holes indicating the formation of pitting corrosion.

![Figure 1](image1.png)

Figure 1. Morphology of aluminum surface (a) before (b) after chemical etching

The effect of the etching concentration on the adhesion force was analyzed by measuring the contact angle of water droplets as shown in Figure 2. The result of contact angle analysis showed that increasing NaNO₃ concentration in the range 0.1 to 0.4 N decreased the Al contact angle. It is shown that the initial increasing of NaNO₃ can stimulate pits nucleation which should enhance uniformly pitted Al surface. Decreasing in contact angle indicates an increase in adhesion force. However, the contact angle has been increased by NaNO₃ concentration further increased. This is due to the higher concentration will cause uncontrollable pitting corrosion thus damaging the desired corrosion structure of Al metal.
3.2. The effect of NaNO$_3$ concentration on resistance and conductivity

The interface resistance between the current collector and the electrode and the internal resistance supercapacitor could influence the charge and discharge processed. The interface and internal resistance for various NaNO$_3$ concentrations can be seen in Figure 3.

The experimental results showed that both the interface and internal resistance are decreased significantly compared without chemical etching. With increasing NaNO$_3$ concentrations up to 0.4 N, the interface and internal resistance have obvious decreased. However, the interface and internal resistance tended to slightly increased by NaNO$_3$ concentration further increased.

As the result shown in Figure 2 and 3, it can be seen that the decrease of contact angle due to etching processed is directly proportional to the decrease of the interface resistance. Increased adhesion forces by a decrease in contact angle may increase the contact area and binding strength between the Al surface and the electrode material. Decreasing the interface resistance will be followed by a decline in the overall internal resistance, as shown in Figure 3. This is due to the inter component of the supercapacitor being an integrated system, hence the decline of resistance from the current collector Al will reduce the overall resistance [3].

The results of the conductivity analysis on various NaNO$_3$ concentrations are shown in Figure 4 which shows that the conductivity is always inversely proportional to the resistance according. This indicates that the smaller the resistance in a material the easier it will be for the mobility of electrons in a material. Conductivity enhancement will improve the charge and discharge processed.
Figure 4. Effect of NaNO$_3$ concentration on conductivity and resistance

3.3. Effect of gamma irradiation dose on functionalization of carboxyl groups, resistance, and conductivity

The basic structure of the graphene oxide (GO) material, especially the surface area and the oxygen group on the surface, affects the properties and performance of the material [18-21]. The number of carboxyl groups for various gamma irradiation doses can be seen in Figure 5.

Figure 5. Effect of gamma irradiation doses on the amount of carboxyl group

The addition of carboxyl groups on the electrode composite surface shows the success of the formation of carboxyl on graphene oxide by cellulose decomposition of PAni-GO-Cellulose-La and hydrolysis reaction of the amide group during the irradiation. An increase in the radiation dose enhances the energy intensity for initiating the formation of radicals and prolonged the propagation step of the chain scission and hydrolysis process, causing to higher the formation of carboxyl.

The effects of gamma irradiation on interface, internal resistance and conductivity were studied at different radiation doses while other influential factors were maintained constant and the results are given in Figure 6 and 7.
The results reveal that initial increasing irradiation dose at 20 kGy has not given significant change both the resistance and the conductivity. Decreasing of the resistance with increasing radiation dose at 40 kGy can be observed then tended to increase by radiation dose further increased. In turn, these result inversely proportional to the conductivity.

As radiation dose increases to a sufficient dose, the conjugations of more carboxyl group become a better ionic mobility in these electrode networks and allow the conductivity to increase until the optimum value. These improvements are due to wettability increasing of the electrode material which provide good contact with the electrolyte solution and facilitate ion mobility. In addition, the irradiation process is also followed by layer peeling to form a thin monolayer electrode material, thereby reducing the electron transfer distance and increasing the contact surface area [14]. However, with radiation doses exceeding 40 kGy, the resistance tended to increase inversely with the conductivity. It might be presumed that the excessive hydrophilicity due to the addition of carboxyl groups can cause particle agglomeration in the electrodes. In addition, excessive carboxyl groups will also damage the sp2 structure of GO in the electrode materials.

4. Conclusion
The results of the supercapacitor characterization which includes testing the interface resistance, internal resistance, and conductivity show an increase in the performance of PANi-GO-Cellulose-Lanthanum-based supercapacitors using chemical etching on Al surface current collector and gamma irradiation. Relatively good conditions were obtained in 0.4 N NaNO₃ etching concentration and gamma irradiation doses at 40 kGy.
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