CHEMICAL ENGINEERING TRANSACTIONS
VOL. 46, 2015

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Peiyu Ren, Yancang Li, Huiping Song

ISBN 978-88-95608-37-2; **ISSN** 2283-9216

DOI: 10.3303/CET1546110

Effect of Aluminum Foil Etching Process on Graphene Super Capacitor

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With rapidly development of the economic and society, environmental pollution become a imminent problem in modern society. Super capacitors as a kind of green energy has a broad application prospect, and the graphene is the most commonly used material in super capacitors. This paper mainly studies the impact of different aluminum foil etching conditions on the performance of graphene super capacitor. This paper take the experiments of aluminum foils under different etching time, solution concentration and current density, then analyze the SEM graph, galvanostatic curve and specific capacitance value of different controlled conditions, finally come to the result that at the 3:1 Cl^- and SO_4^{2-} solution concentration ratio, 70mA/cm^2 current density and 140s etching time, the graphene super capacitor has the maximum specific capacitance of 115F/g.

1. Introduction

In order to meet the needs of modern society and take into account of the environmental and energy security, there have been an increasing demand of super capacitor technology worldwide. Super capacitor fill the gaps between traditional capacitor and battery, with higher charge power than conventional capacitors, at the same time it can provide greater energy density than traditional battery, Tur, V(2013) reported. At present, countries around the world including the United States, Russia, Japan and so on all has invested the super capacitor research and development a lot of manpower and material resources, and the corresponding super capacitor development plan, in the foreseeable future, will get rapid development.
Equivalent series resistance (ESR) in current collector is one of the main indexes influencing the performances of super capacitor, the existence of the ESR in current collector can lead to the reduced charge range and weakened storage capacity. Because of the high conductivity, low resistance and low price, the aluminum foils become the first choice of current collector materials, thus the etching process of the aluminum foils will greatly effect the overall performance of the super capacitor, Dian Bo et al (2013) reported.

2. Effect of aluminium foil etching process on graphene super capacitor

Aluminum foil etching method mainly has three ways: physical method, chemical etching, and electrochemical etching. These three methods are in order to increase the density of the aluminum foil corrosion on the surface of the hole and make its uniformly distributed, but the premise is the aluminum foil mechanical strength cannot significantly reduced, otherwise it will cause a decline in the super capacitor performance.
Physical method is the first to be used while it’s the roughest methods. By using different particle size of sand paper or brush friction surface to the aluminum foil, in order to increase the corrosion on the surface of the hole density. Physical processing of aluminum foil surface corrosion hole size is larger, the depth is shallow, and because of the influence of human factors, the corrosion hole distribution is very uneven. It is one of the worst corrosion effect of the three.
Chemical etching use the chemical property of aluminum and acid. By putting aluminum foil in acid or alkali solution, erosion holes will form on the surface of aluminum foil. But most of the aluminum foil in the alkali solution reacted of parallel to the surface of aluminum foil a very uniform dissolution process, which can lead to aluminum foil surface gradually thinning, this can also lead to low etching effect. And chloride ion is

Please cite this article as: Cheng S.J., 2015, Effect of aluminum foil etching process on graphene super capacitor, Chemical Engineering Transactions, 46, 655-660 DOI:10.3303/CET1546110

strongest among corrosive of anion, aluminum foil in halogen acid solution is very easy to produce surface localized dissolve, and form a certain shape of corrosion hole, so halogen acid corrosion is considered to be the best aluminum foil etching solution. But relative to the electrochemical etching, the dissolution of aluminum foil speed in acid solution is much lower, it has a limit on the application range of the chemical etching.
Electrochemical etching is developed on the basis of chemical etching, by increasing the electric field, and quicken the process of aluminum foil etching. In the electrochemical etching, the applied electric current density is proportional to the dissolution rate of aluminum foil, so we can adjust the density of impressed current to control the speed of aluminum foil etching.
This paper adopts H_2S0_4-HCl as corrosion solution used on aluminum foil etching, and the paper explore the etching conditions on the graphite matrix of super capacitor, aim to find the optimal etching method to optimize the preparation of graphene based super capacitor.

3. Effect of aluminium foil etching time on the graphene super capacitor performance

Aluminum foil will be cut into certain size at first, clean the aluminum foil surface with 1mol/L NaOH solution, then wash with deionized water, put the aluminum foil in 2 Cl- :4 SO42- etching solution after natural drying with a temperature of 70 ° C and current density of 50mA/cm2, the etching time will set respectively at 100s, 120 s and 140 s, 160 s and 180 s, the etching time of 180s will be not be discussed because of at the etching time of 180s the aluminum foil intensity is significantly reduced.
The aluminum foil will be washed with deionized water after etching, and scanned with electron microscope while dry and clean to observe the foil surface, as shown in Figure 1.
As shown in Figure 1, as the extension of etching time, the etching degree of the aluminum foil surface increased.
At the etching time of 100 s, aluminum foil surface corrosion is very uneven, most of the area are not corrode. At the etching time of 120 s, although the holes number increased, but still can't fully distribute on the surface. When the etching time is extended to 140s and 160s, the corrosion is relatively complete. At the etching time of 140s, the number of apertures on the aluminum surface has dramatically increased, and the apertures covers the most part of aluminum foil surface, while at the etching time of 160s, which can be seen from the Figure 1-d, a lot of apertures on the surface of aluminum foil mild together, grew up as bigger apertures, meaning an excessive corrosion which reduce the aluminum foil's strength and so forth the performance of the capacitor.

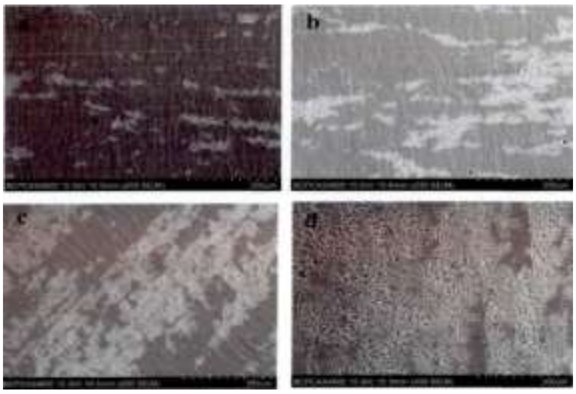

Figure 1: The SEM of aluminum foil surface with different corrosion time: a.100s b.120s c.140s d.160s

With the 4 kinds of aluminum foil of different corrosion time, prepare the graphene super capacitor, and take the galvanostatic test, the test results are shown in the figure 2.
In figure 2, curve W represents a super capacitor's galvanostatic curve with the aluminum foil without etching. As can be seen from the figure, the performance improvement of the supercapacitor of galvanostatic curve W and 100s differs very little, and for the etching time more than 120s, the performance of the super capacitor has obvious improvement, charge and discharge time significantly extend. The result is that with the increase of etching time, etching aperture density and depth increases, make the contact between active material and aluminum foil better, thus effectively reduce the equivalent resistance.
Based on the super capacitor specific capacitance formula, without preparation of aluminum foil etching, the capacitor specific capacitance is 16 F/g, with the etching time of 100s, 120s, 140s and 160s, the specific capacitance of the super capacitor is 19.7 F/g, and F/g, 54 F/F/g and 48.7 g, as shown in Figure 3, which shows that the super capacitor specific volume as the etching time increase showed a trend of decrease after

the first increase, at the etching time of 140 s, the specific capacitance reach the maximum value, with the etching time rise over 140s, the specific capacitance drop down as the apertures milt to bigger apertures.

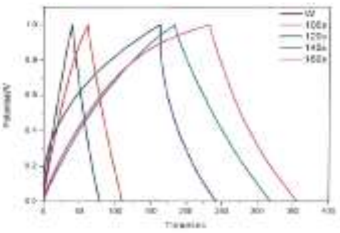

Figure 2: The galvanostatic curve of super capacitor with different aluminium foil etching time

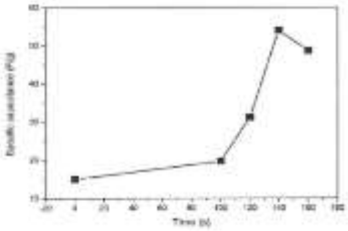

Figure 3: The specific capacitance of super capacitor with different etching time

4. Effect of aluminium foil etching solution concentration ratio on the graphene super capacitor performance

Cut the aluminum foil into a certain size, clean with 1mol/L NaOH solution, wash with deionized water, and natural dying, then put the aluminum foil in the HCL, H_2SO_4 solution with different concentration of 2:1, 3:1 and 4:1, with etching time of 140s, etching temperature at 70OC. After etching, wash aluminum foil surface with deionized water and nature dry the foil, observe the aluminum foil surface with electron microscope, the SEM result is shown in Figure 4.

Figure 4-a is the SEM graph of none etched aluminum foil, Figure 4-b is the aluminum foil etching under a concentration ratio of 2:1 HCL and H_2SO_4 solution, Figure 4-c is the aluminum foil etching under a concentration ratio of 3:1 HCL and H_2SO_4 solution, Figure 4-d is the aluminum foil etching under a concentration ratio of 4:1 HCL and H_2SO_4 solution.

Comparing of the four graphs, with the etching solution of concentration ratio of 2:1, the corrosion on the aluminum foil surface is not complete, none corrosion areas exist. With the etching solution of concentration ratio of 3:1, the aluminum foil surface etching degree aggravating gradually, the aperture distribution is more uniform, the distribution density has increased significantly, but when the concentration ratio change to 4:1, although the aperture on the aluminum foil surface become more intense, a lot of apertures milt together and collapse.

In figure5, the charge and discharge current density of 0.2A/g, and from the galvanostatic curve the follow conclusion can be drawn: all the performance of super capacitor has been raised after the aluminum foil etching, but at the concentration ratio of 2:1, the performance doesn't change too much, at the concentration ratio of 3:1 and 4:1, the galvanostatic time greatly extended, shows a larger specific capacitance, compare to the status under concentration ratio of 2:1, also an obvious drop at the voltage value at discharge instance.

From the galvanostatic graph, the calculated results of specific capacitance under different etching solution concentration ratio is 16F/g, 54F/g, 68F/g, and 52F/g, as shown in figure 6.

From figure 6, the etching solution with concentration ratio of 3:1 have the maximum specific capacitance, thus the super capacitor has the best performance. The reason of specific capacitance change in different etching solution is that during the etching process, the etching core first formed on the aluminum surface, the etching reaction happens in the aperture first generate Al^{3+} ion to fill the aperture, with the increase concentration of Al^{3+} in the aperture, the Cl^- ions outside the aperture will diffuse into the aperture to reach electrical balance, results a deeper and wider aperture because of the corrosion in the aperture, the consequences are decrease in specific surface area and strength, increase in resistance, Peng, N. et al (2014) reported. The consequences will all lower the performance of the super capacitor.

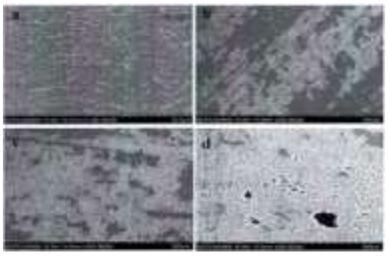

Figure 4: The SEM of aluminum foil surface with different etching solution concentration a. Unetched Aluminum Foil b.2:1 c.3:1 d.4:1

The galvanostatic graph of the above four kinds of aluminum foil super capacitor is shown in Figure 5.

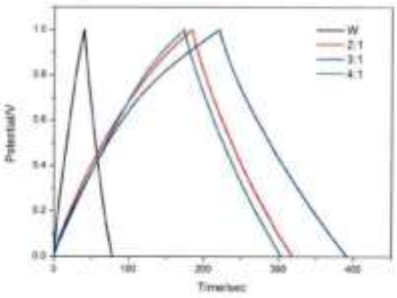

Figure 5: The galvanostatic curve of super capacitor with different aluminum foil etching solution concentration

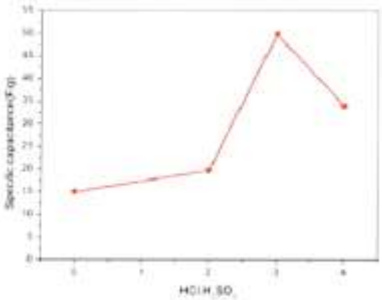

Figure 6: The specific capacitance of super capacitor with different etching solution

5. Effect of aluminium foils etching current density on the graphene super capacitor performance

First cut aluminium foil into a certain size, clean with 1mol/L NaOH solution, wash the aluminium foil surface with deionized water, then put the foils into the HCl H2SO4 after natural drying, the concentration ratio of the solution is 3:1, with etching time of 140s and a temperature of 70OC, set the etching current density to 30mA/cm2, 50mA/cm2, 70mA/cm2 and 90 mA/cm2. Clean the aluminum foils surface with deionized water after the etching and natural drying the foils, then put the foils under electron microscope, shown in figure 7.Ferrari, A. C. (2013) reported. The figure 7-a is the SEM graph of aluminum foils surface with etching current density of 30mA/cm2, the follow graph of figure 7-b, 7-c and 7-d is the SEM graph of aluminium foils surface with etching current density of 50 mA/cm2, 70 mA/cm2 and 90 mA/cm2.

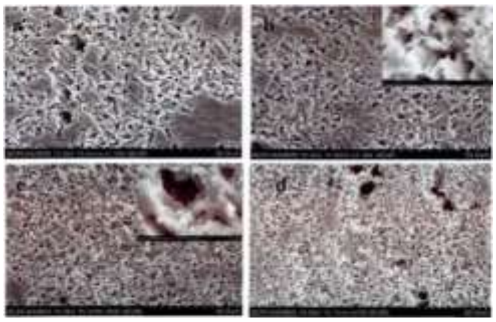

Figure 7: The SEM of aluminum foil surface with different etching current density: a. 30mA/cm^2 b.50mA/cm^2 c.70mA/cm^2 d.90 mA/cm^2

In figure 7, it can be seen that when the current density is 30 mA/cm2, the apertures on the foils surface scatter distributed with different aperture diagram, when the current density increased, the apertures distribute more evenly and its numbers also raise, but at the current density of 90mA/cm2, aluminum foil surface obviously shows aperture perforation and milt together, aluminum foil thickness thinning greatly, general corrosion happened on the aluminum foil, this can cause a decline in the performance, because on the one hand, the aperture milt together restrict the aperture enlarge, on the other hand, this corrosion can cause stress concentration in the process of bending, results the decrease in the bending strength and strength of the aluminum foil. The causes of this phenomenon is the high current density, make the aluminum foil and solution corrosion reaction too fast, before the aperture core can enlarge hole, other solution out of aluminum foil surface will dissolve in the fluid of the corrosion, and aluminum foil surface will collapse, Ban, C et al (2014) reported. With etching current density of 50 mA/cm2 and 70 mA/cm2, the apertures on the aluminum surface distribute evenly and have the maximum diagram, Peng, N et al (2014) reported. At the current density of 70 mA/cm2, shows the deepest aperture in figure 7, it's a great advantage for graphene materials to adhere.

The galvanostatic test results of the super capacitor with current collector made by the above four kinds of aluminum foils are shown in figure 8.

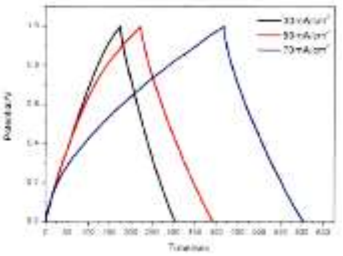

Figure 8: The galvanostatic curve of super capacitor with different aluminum foils etching current density

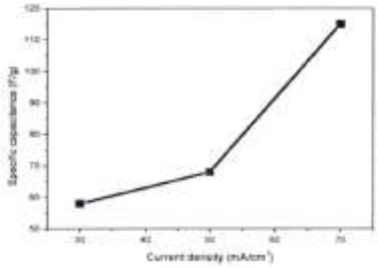

Figure 9: The specific capacitance of super capacitor with different current density

The aluminum foils at current density level of 90 mA/cm2 is no longer suitable for the current collector, because the foils become easy to break. All the other three galvanostatic curves form three good symmetry isosceles triangles, shows a good reversibility of these three aluminum foils. As the current density increase, the super capacitor's charge and discharge time increase, based on the specific capacitance formula, the specific capacitance of different current density of 30mA/cm2, 50mA/cm2, and 70mA/cm2 is 58F/g, 68F/g, and 115F/g, as shown in Figure 9.

As shown in figure 9, with the current density of 70mA/cm2, the corresponding specific capacity of super capacitor have the maximum value, the result is same as the analysis of the SEM graph above. Under the current density of 30mA/cm2, compared with other two kinds of aluminum foil, its corrosion aperture density is not big enough, and the distribution of the aperture is not even. Under the current density of 50mA/cm2, the corrosion apertures are shallow compare to the apertures under the current density of 70mA/cm2, thus the active substances such as graphene cannot fully adhere. Therefore, the processing current density of 70mA/cm2 is the most appropriate current density.

6. Conclusion

This paper mainly studies the impact of different aluminum foil etching conditions on the performance of graphene super capacitor.

Capacitance of aluminum foil for electrochemical etching at the ratio of 2:1 in Cl^- and $S0_4^{2-}$ solution, with corrosion temperature of 70° C, under the condition of current density for 50mA/cm^2, aluminum foil etching time set to 100s, 120s, 140s and 160s, the etching time of 140s has the maximum specific capacitance which is 54 f/g.

At the etching time of 140 s, etching temperature of 70 °C, under the condition of current density for 50mA/cm^2, respectively select Cl^- and $S0_4^{2-}$ concentration ratio of 2:1, 3:1 and 4:1 for aluminum foil etching solution and test their electrochemical properties, the results show that when the concentration ratio of 3:1, the corresponding super capacitor has the highest specific capacitance 68 f/g.

At the Cl^- and $S0_4^{2-}$ concentration ratio of 3:1, etching time of 140S, etching current density respectively as 30mA/cm^2, 50mA/cm^2, 70mA/cm^2 and 90mA/cm^2, the final result show, at the current density of 70mA/cm^2, specific capacitance reached 115 f/g.

To sum up, the optimum process parameters of aluminium foil etching is with Cl^- and $S0_4^{2-}$ concentration ratio at 3:1, the etching current density at 70mA/cm^2, etching time of140 s, the graphene super capacitor has the maximum specific capacitance of 115F/g.

Acknowledgements

This work was financially supported by The Project of the key discipline of theoretical physics of Xinxiang University.

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