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Electrochemical Properties of Aluminum-Graphene Composite Anodes

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Properties of several aluminum-graphene composites obtained by three different methods are investigated by Raman spectroscopy, SEM and electrochemical techniques . A two-phase synthesis method under halide melt above the melting point of aluminum yielded the most uniform distribution of graphene flakes in the metal matrix. It is shown that anodic polarization of the Al-graphene composites is different from pure aluminum and dramatically depends on the method of composite synthesis. Composites with uniform distribution of graphene flakes possessing improved electrochemical properties can be considered as perspective anode materials for an aluminum-air battery.

Keywords: Aluminum, graphene, composite, electrochemistry, aluminum, battery

1. INTRODUCTION

Metal-air batteries with aluminum anodes have received particular attention [1] because of their high theoretical energy density, possible low dependence of the internal resistance on temperature, projected low raw material and fabrication cost and related environmental friendliness. The last assumption is based on the fact that of the battery components are non-toxic and have high recyclability. Indeed, aluminum metal has very large theoretical energy density (8100 Whkg^{-1}), if used as an anode material, and high negative standard potential (-2.37 V vs. SHE). It is lightweight (2.71 g cm^{-3}) and is the third most abundant element in the earth crust [2-5].

However, aluminum surface is covered by dense protective oxide film, which effectively passivates it, thus, slowing drastically electrochemical processes in aqueous media. This mostly results in a high anodic dissolution overvoltage, leading to a drastic decrease of the cell energy density. This electrochemical behavior limits the use of aluminum metal as an anode material in battery applications [6, 7].

The formation of aluminum oxide film on a surface causes the phenomenon of so-called ‘‘delayed action’’. That is the time lag before the cell reaches its maximum operating voltage when the circuit is closed [4]. To decrease the polarization caused by such oxide film effects, considerable effort has been made to develop aluminum alloy anodes and electrolyte additives for aluminum batteries with aqueous electrolytes, especially for aluminum-air batteries [8, 9].

It is well known that aluminum-graphite and aluminum-graphene composites possess improved mechanical and thermal properties combined with somewhat lower corrosion resistance comparing to a pure aluminum due to discontinuities in the oxide film. Specifically, such surface defects increase the number of sites where metal dissolution can be initiated [10-12]. The latter feature of Al-carbon composites, unwanted for construction materials, may be of importance in batteries. This property may lead to a lower polarization of the aluminum anode, increasing the overall cell voltage and energy density. To the best of our knowledge, no information on the behavior of aluminum-carbon composites in the aluminum-air or aluminum-ion batteries has been reported yet.

There is a limited number of papers on the electrochemical properties of aluminum-graphene composites [10]. The latter are reasonably assumed to be strongly determined by the method of the synthesis. The most evident way to obtain aluminum-graphene composite is alloying or sintering of pure initial reagents, thus, most of the available reports are based on those processes. Since aluminum and carbon do not form solutions, intermetallic or intercalation compounds [13] the uniformity of distribution of carbon inclusions in aluminum metal remains questionable [14].

At the same time in the last ten years various methods of metal-graphene composites have been developed. Various forms of carbon compounds (et. fullerenes, carbon nanotubes, graphene formulations) are commercially available and, thus, can be used for doping aluminum. As it was mentioned above, the electrochemical properties of resulting composite materials must strongly depend on the distribution of a dopant in the metal matrix.

One of the most promising approaches to obtain uniform metal-graphene composites is that the graphene species are formed within a molten halide matrix directly in contact with liquid metal [14]. Specifically this method is based on thermal decomposition of non-volatile organic compound in the salt melt. Upon deep decomposition a chemical interaction of residual organic substances with surface of melted aluminum takes place resulting in the formation of graphene flakes. Overall, such synthesis of a graphene-aluminum composites looks very promising showing uniform graphene distribution within the metal matrix [14].

We aimed to compare electrochemical properties of aluminum-graphene composites obtained by a conventional "shake-and-bake" approach and the same composites synthesized via a novel heterogeneous process under a molten halide matrix. Specifically, we studied anodic dissolution rate of aluminum anodes, which is of utmost importance in primary and secondary galvanic cells based on aluminum chemistry.

2. EXPERIMENTAL METHODS

2.1. Materials and Chemicals.

Aluminum powder (4N, >99,999% purity), glucose, sodium hydroxide and all salts were purchased in the highest quality available from NeoLab (Bangkok, Thailand). Deionized water was obtained with a Milli-Q purification apparatus.

2.2. Synthesis of aluminum-graphene composites.

Three different composite specimens were synthesized.

The first one was obtained by a direct fusion of an aluminum-graphene powder mixture. The synthetic procedure for obtaining graphene through a graphene oxide precursor was described elsewhere [15]. The resulting product was mixed with aluminum powder (2% wt/ of graphene) using a benchtop ball mill Emax by Retsch, Düsseldorf, Germany) and compressed (at 1000 bar) at ambient temperature. The total weight of aluminum-graphene pellets was ca. 100-120 g. The pellets were heated using muffle furnace (MTI Corp., Richmond, CA, USA) up in alumina crucibles using a temperature elevation rate of 10 degrees per minute. As the temperature reached 800^{0}C the reaction mixture was kept ant this temperature for one more hour. Intensive stirring was provided using a tungsten agitator. During the whole process an argon supply was carried out inside the furnace to protect the reaction mixture from oxygen. Finally, the reaction mixture was cooled down. Resulting composite samples were assigned a name Al-Gr1.

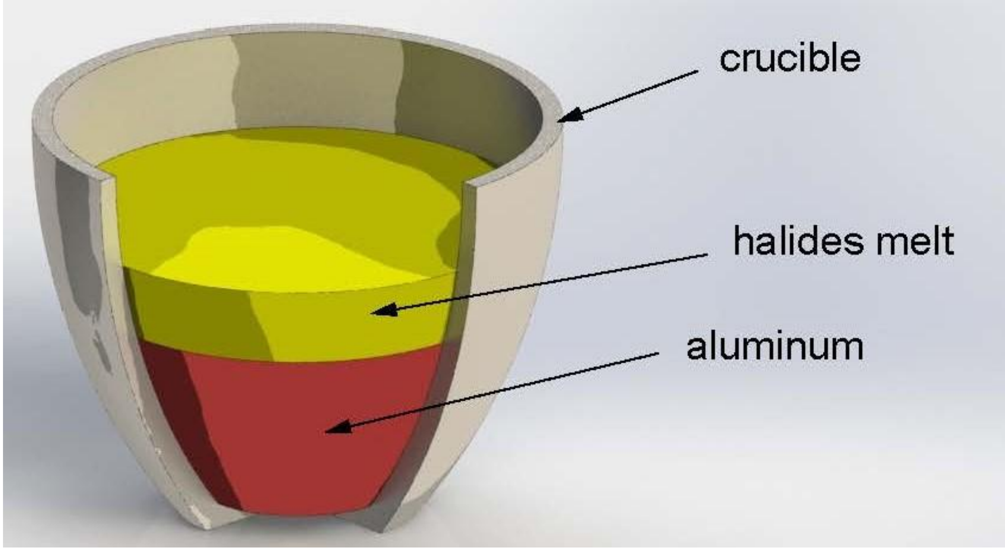


Figure 1. A graphical representation of two-phase heterogenous synthesis of aluminum-graphene composites (Al-Gr2 and Al-Gr3)

The second type of aluminum-graphene composite (Al-Gr2) was produced according to the next procedure. Reaction mixture was made with 50 g of aluminum powder, 65.5 g of dry LiCl, 183.5

g of dry NaCl and 2.5 g of glucose. All substances were carefully mixed, and resulted mixture was put in an alumina crucible, which was placed in a muffle furnace. The reaction mixture was heated with temperature elevation rate of 10 degrees/minute in an argon atmosphere. After the temperature had reached 600^0C, the reaction mixture was kept ant this temperature level for one hour without agitation. This temperature exceeds the melting point of halide mixture, but is below the melting point of aluminum metal. Finally, the reaction mixture was cooled down to ambient temperature and immersed in water. After salts dissolution aluminum-graphene composite was extracted by the filtration in a form of a powder. Flat electrode was made from the powder obtained by 1000 bar pressing under 400^oC.

Aluminum-graphene composite (Al-Gr3) was obtained from a reaction mixture containing 100 g of aluminum powder, 55 g of dry LiCl; 145 g of dry KCl; 0 or 5.0 g of glucose. All substances were carefully mixed and heated up with the rate of 10 degrees per minute under argon flow. After the temperature had reached 800^0C, the reaction mixture was kept ant this temperature for one more hour. Intensive stirring was provided using titanium agitator. Finally, the reaction mixture was poured in water and the aluminum-graphene composite ingot was extracted. Fig.1 contains a graphical representation of two-phase heterogenous synthesis of a aluminum-graphene composites.

Regardless of the synthetic procedure the composite was machined in a form of flat disks 22 mm in diameter with various thickness (3-5 mm) with a benchtop lathe (Sherline Corp, CA, USA). Before characterization and electrochemical measurements the samples were sanded 3M polishing papers (3-0.3 μm), immersed and sonicated for 1 min in 1 M NaOH at 60°C in order to clean the surface, and, finally, rinsed with deionized water.

2.3. Methods of characterization.

XRF analysis (S2 Puma, Bruker BioSpin AG, Bangkok, Thailand) was used to confirm an average carbon content in the resulting aluminum-graphene composites. For the XRD determination five samples of each specimen were used. Raman spectroscopy was used to confirm the graphene formation in the metal matrix with RamMics M532 Raman Microscope (Enhanced Spectrometry, Inc., San Jose, CA, USA). The Raman spectra were recorded with a 532 nm excitation laser.

In order to characterize surface morphology of composites and study graphene distribution SEM images were obtained with PhenomProX (NanoScience Instruments, Alexandria, VA, USA)

2.4. Electrochemical measurements.

All the electrochemical experiments were performed by using Electrochemical Analyzer/Workstation (Model 660E Series, CHI Instruments, China). The electrodes were fixed with a clamp and sealed by o-ring of 3/4-inch in diameter. The polished side of the electrode was exposed to the solution.

Afterwards the electrodes were rinsed with a deionized water and placed in a cell for electrochemical measurement. Three-electrode electrochemical cell made out of polycarbonate was used for electrochemical measurements (Fig.2). An Al electrode (either pure or composite) was used as a working electrode. The diameter of the working electrode was 1/2 inch with a total exposed surface area of 1.27 cm^2.

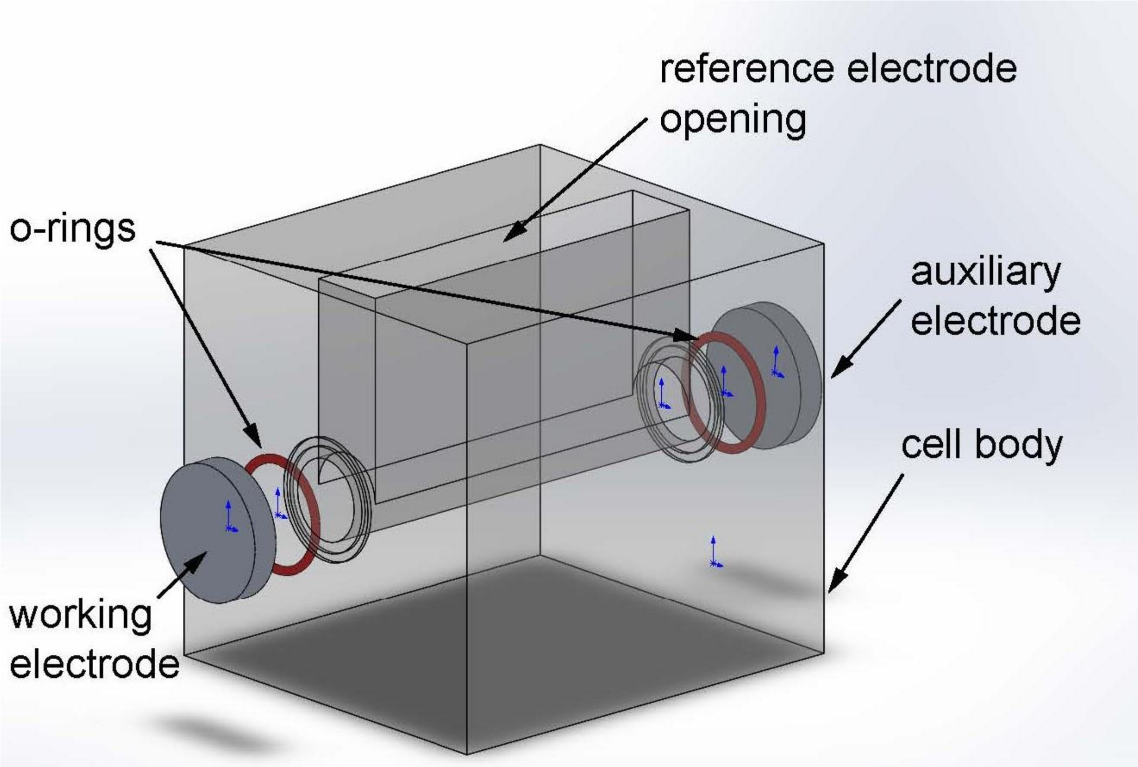


Figure 2. Polycarbonate three electrode electrochemical cell (for clarity the refernce electrode is not shown).

An Ag/AgCl electrode (in 3 M KCl, CHI Instruments) and a platinum foil disk were employed as reference and counter electrodes, respectively. Both working and counter electrodes were held with two insulated clamps opposite to each other. A solution of 3.5% sodium chloride was used as electrolyte. The galvanostatic tests were carried out at anodic current density in the range of 20–100 mA cm^{-2} on samples during a 60 min period. During the anodic polarization variation in the potential was recorded as a function of time.

The volume of the solution used in the tests was always 100 ml. All measurements were also carried out at ambient temperature (25 ± 0.1°C) in freely aerated solutions.

3. RESULTS AND DISCUSSION

3.1. Surface morphology.

According XRF studies Al-Gr1, Al-Gr2 and Al-Gr3 contained 2.0±0.2, 1,5±0.2 and 3±0.2 % wt. of carbon, correspondingly. All three methods of synthesis apparently showed a very consistent yield of carbon species in the aluminum matrix.

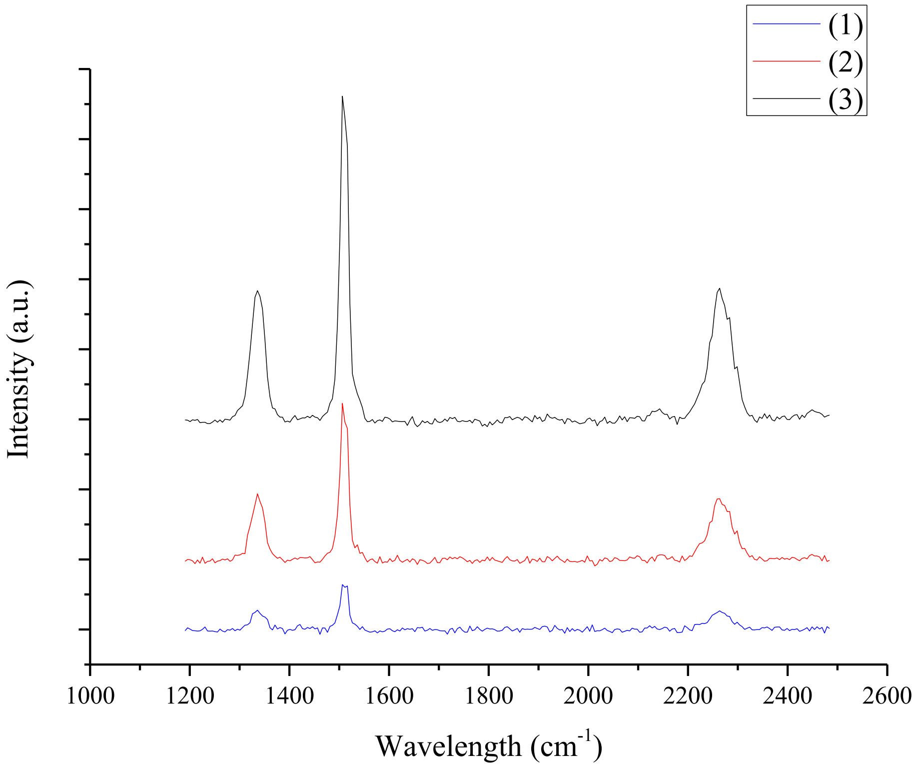


Figure 3. Raman spectra of Al-graphene composites for Al-Gr1 (1), Al-Gr2 (2) and Al-Gr3 (3) specimen respectively.

The Raman spectra of Al-graphene composites (Fig.3) clearly showed the Stokes phonon energy shift caused by laser excitation of graphene, which creates two main peaks in the Raman spectrum: 1520 cm^{-1}, a primary in-plane vibrational mode, and 2280 cm^{-1}, a second-order overtone of a different inplane vibration 1330 cm^{-1}. The position of a peak at 2280 cm^{-1} corresponds to the multilayered disordered graphene [16]. Increasing intensity of a peak at 1520 cm^{-1} likely corresponds to the increasing number of single layered graphene flakes in the sample.

As we mentioned above, the distribution of graphene strongly depends on the synthetic procedure. We used SEM to characterize the composites. Surprisingly, the Al-Gr1 composite, which was obtained as a direct fusion of aluminum and graphene powders, demonstrated very poor uniformity of graphene clusters in the metal matrix. We were not able to find a region as large as 100x100 μm in which even a moderately uniform distribution can be observed. Graphene formed relatively large clusters ranging from 50 nm to 200 □m.

At the same time from a surface morphology of composites Al-Gr2 and 3, which is shown in Fig.4, one may conclude that the distribution of graphene clusters is rather uniform. The flakes of graphene can be seen in images C and D. Among three specimen the surface of Al-Gr3 samples demonstrated the most consistent distribution of relatively (B) small graphene inclusions of 3-20 μm across. The shape of single and multilayered graphene flakes is shown in Fig3D image. It should be emphasized that even for Al-Gr3 composite graphene distribution is represented by scattered graphene clusters of finite size.

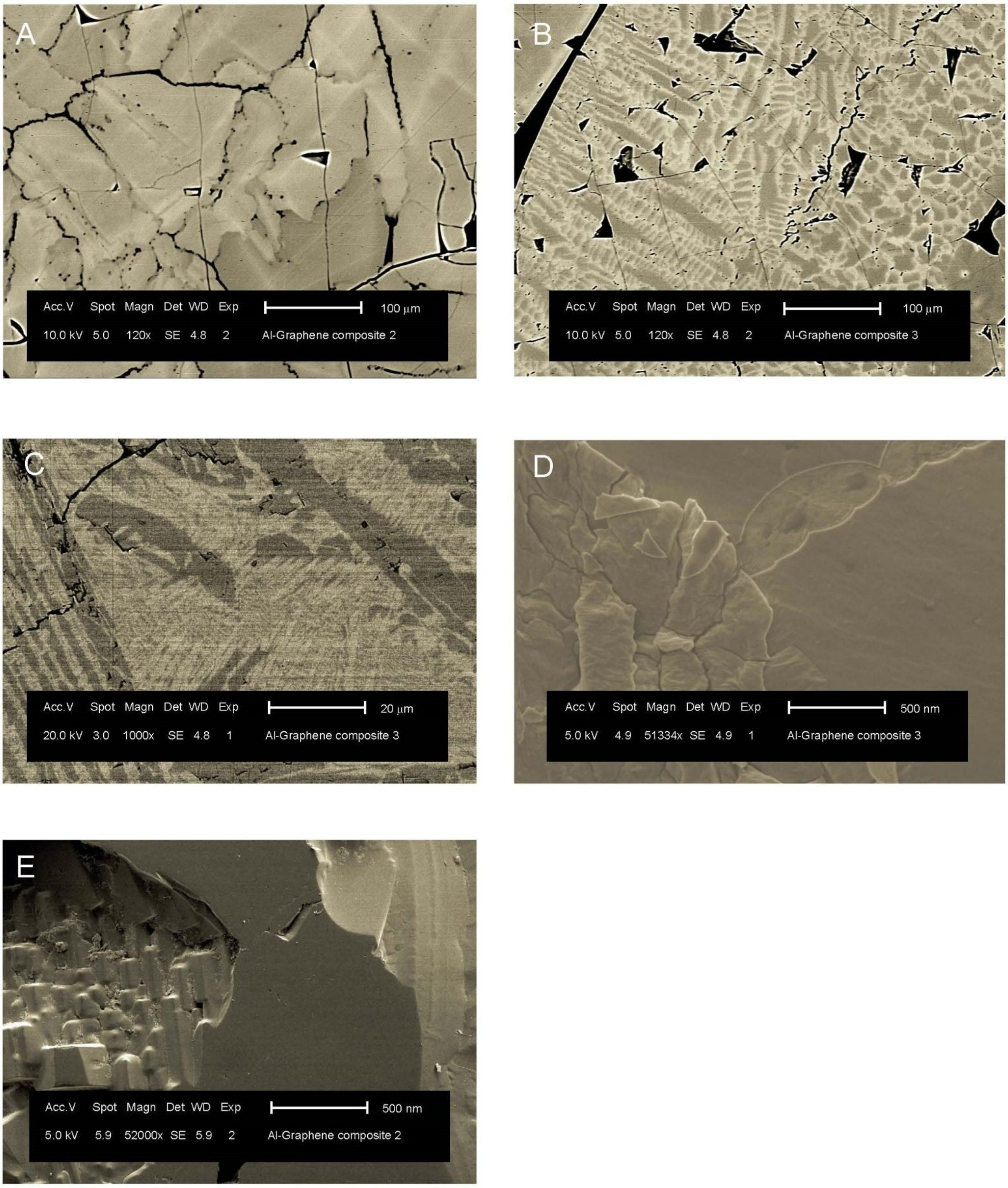


Figure 4. The SEM images of surface morphology Al-Gr2 (A, E) and Al-Gr3 (B, C and D) composites using different magnification.

Both Raman and SEM studies strongly suggest that Al-Gr3 specimen possess the most uniformly distributed graphene flakes with the smallest number of layers.

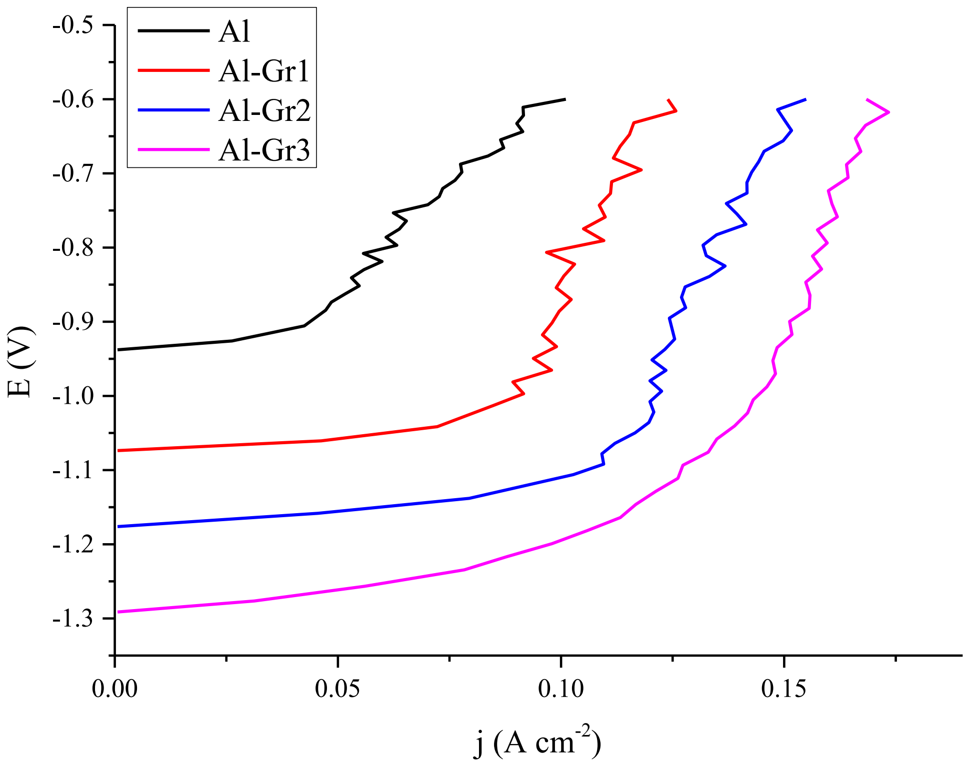


Figure 5. Anodic potentiodinamic polarization curves of Al and Al-Gr1, Al-Gr2, Al-Gr3 composites in 3.5 wt% NaCl solution.

3.2. Electrochemical studies.

3.2.1. Potentiodynamic polarization.

In order to evaluate anodic dissolution rate of each aluminum-graphene composite a potentiodynamic polarization test was carried out using a three electrode cell system. The potential was swept at 0.1 mV s^{-1} scanning rate from an initial potential of the open-circuit (OCP) to a final potential of -0.6V vs. Ag/AgCl. Fig.5 shows the anodic polarization curves of the pure Al and Al-graphene composite samples in 3.5 wt% NaCl solution.

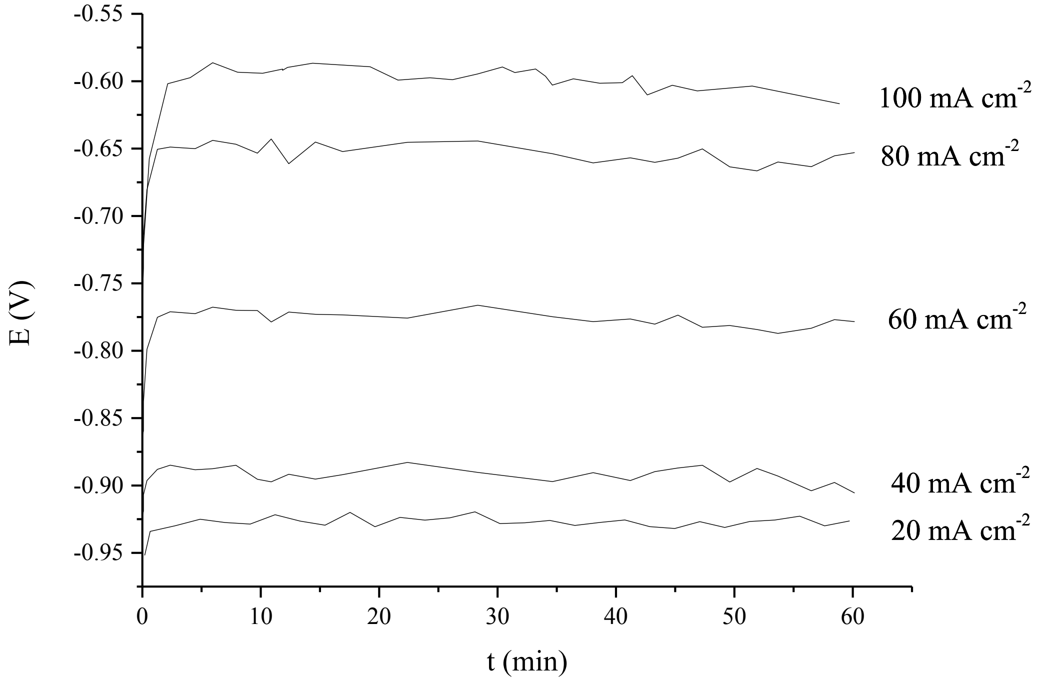
The addition of graphene to aluminum produced considerable negative shift of the OCP for all composites and shifts the potential of Al dissolution towards the negative direction. At given potential within the whole potential window the anodic current densities of all Al-Graphene composites dissolution are higher than that of Al pure.

On all polarization curves two regions with different slopes are observed. At low current densities dissolution proceeds at almost constant potential, close to corrosion potential of the composite. At higher current densities (>50 mA cm^{-2} for pure Al and >100 mA cm^{-2} the slope of the I-V curve is changed and the reaction rate becomes influenced by an overvoltage, which apparently is related to the reaction interface resistivity caused by the formation of aluminum hydroxide layer [17].

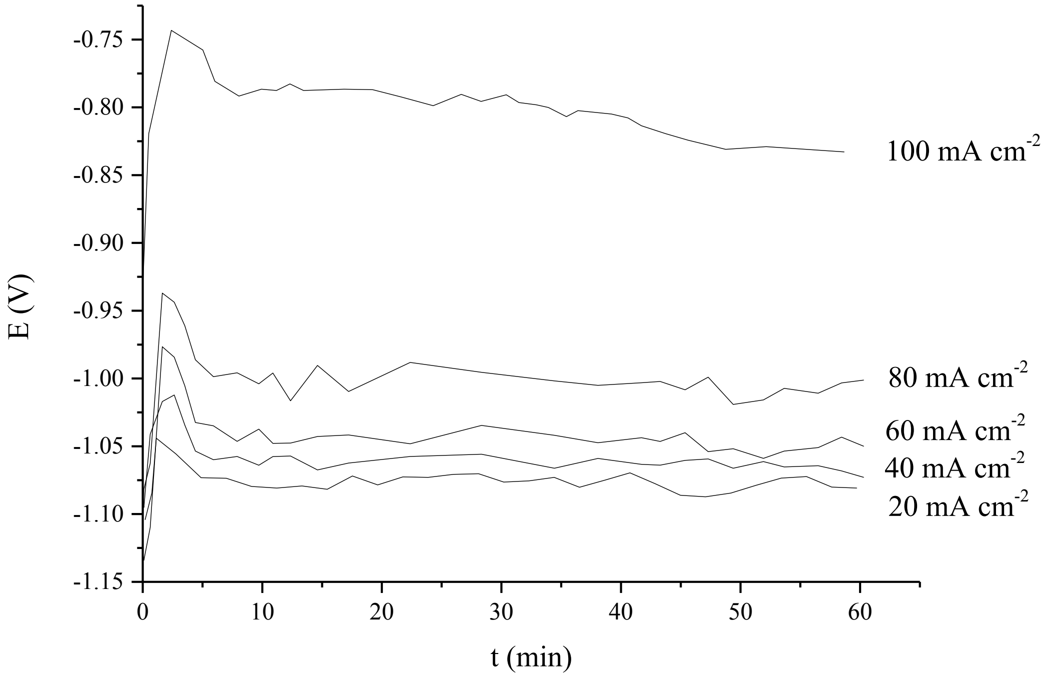
The Al-Gr1 composite exhibits dissolution potential approximately 0.13 V more negative than that of aluminum in the same solution, while that of Al-Gr3 corrosion potential was about 0.36 V more negative. Such difference becomes even higher at the electrode polarization. Therefore, the active dissolution of the composites occurs at much lower electrode polarization so that the polarization of the examined electrodes decreased in the order: Al, Al-Gr1, Al-Gr2, Al-Gr3.

It allows us to conclude that Al-graphene composites have similar electrochemical properties to those of aluminum-graphite composites described by Saxena et al. [11] Higher corrosion rate of Al-Gr composite than the aluminum itself is possibly due to the graphene particles being cathodic relative to the metal matrix thus leading to galvanic corrosion in the presence of an electrolyte. From the power source point of view, the lower dissolution potential means the higher power output of the battery. For example, the air cathode of working prototype of Al-air saline battery has the potential of -0.2 V [18]. If the same cathode is used, the anodic potential of pure aluminum dissolution at 100 mA cm^{-2} current (c.a. -0.6 V) corresponds to cell voltage 0.4 V and power density 40 mW cm^{-2}. For the best composite Al-Gr3 dissolution potential at the same conditions is -1.25 V, giving cell voltage -1.05 V and power density 105 mW cm^{-2}, which is 2.5 times higher than expected in the case of pure Al.

3.2.2. Galvanostatic test.

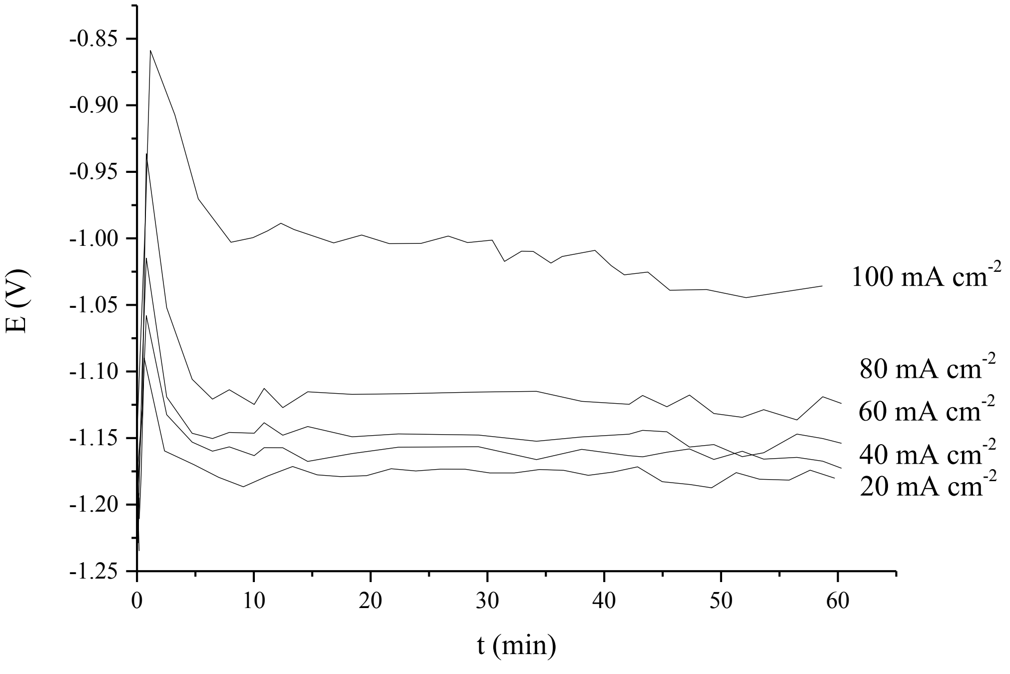


A



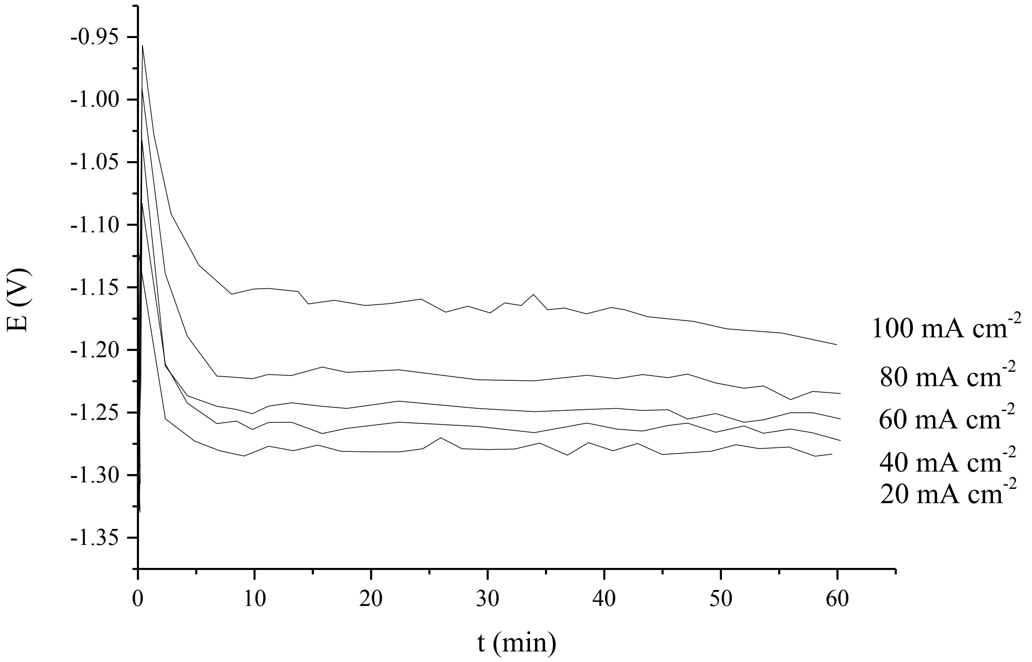
E (V)
-0.75
-0.80
-0.85
-0.90
-0.95
-1.00
-1.05
-1.10
-1.15
0
10
20
30
40
50
60
t (min)
100 mA cm^{-2}
80 mA cm^{-2}
60 mA cm^{-2}
40 mA cm^{-2}
20 mA cm^{-2}

B



E (V)
-0.85
-0.90
-0.95
-1.00
-1.05
-1.10
-1.15
-1.20
-1.25
0
10
20
30
40
50
60
t (min)
100 mA cm^{-2}
80 mA cm^{-2}
60 mA cm^{-2}
40 mA cm^{-2}
20 mA cm^{-2}

C



D

Figure 6. Potential-time responses recorded for pure Al (A), Al-Gr1 (B), Al-Gr2 (C), Al-Gr3 (D) composites in 3.5 wt% NaCl solution at different current densities.

Fig.6 shows the chronoamperometric curves of Al and Al-Gr1, Al-Gr2, Al-Gr3 composites in 3.5 wt% NaCl solution under galvanostatic anodic polarization by currents within the range of 20–100 mA cm^{-2}. After the initial increase of the potential, caused by pseudo-ohmic resistance and a subsequent charging of interfacial capacitance [19], potential of the dissolution of the aluminum samples is attaining steady values, i.e. to the potential plateau of active anodic dissolution [19],. In the case of Al-Gr composites, potential increases up to a certain maximum value and then decreases to the potential plateau of active anodic dissolution. The steady state potential of all samples increased with current densities, practically coinciding with the values, observed in potentiodynamic polarization curves (Fig. 5). The addition of graphene to aluminum in all cases leads to a considerable shift of the steady state potential towards the negative direction. The polarization of the examined electrodes decreased in the order: Al>Al-Gr1>Al-Gr2>Al-Gr3. According to this data, increase of the graphene content leads to better electrochemical performance of Al-Gr anode. It should be mentioned that the lowest electrode polarization is observed for Al-Gr3 composite, which exhibits potential of about 0.2 V more negative than that of aluminum in the same solution at 20 mA cm^{-2}, while this difference is increased to 0.55 V at current density of 100 mA cm^{-2}. The observed dissolution potential difference between pure Al and composite is higher than that for Al–In alloy, which is common anode material for Al-Air batteries [20], and only 0.1 V less than one of Al–Sn [20] or Al-Ga-St-Mg [18] alloys, which are the most promising materials for Al-air power sources to date.

4. CONCLUSIONS

In this article, we present the synthesis and electrochemical characterization of four different electrodes including those of pure Al and Al-Gr composites as anode materials for prospective aluminum-air batteries with sodium chloride electrolyte. Three synthetic methods were evaluated: direct fusion of aluminum and graphene above the metal melting point (Al-Gr1), two phase heterogeneous synthesis of graphene flakes in the metal matrix below the metal melting point (Al-Gr2) and the same method above the melting point of aluminum (Al-Gr3). Both Raman and SEM studies strongly suggest that Al-Gr3 specimen possess the most uniformly distributed graphene flakes with the smallest number of layers.

The electrochemical results reveal that all Al-Gr composites possess reduced anodic electrode polarizations, thus, increasing the expected cell voltage. Direct sintering of graphene with aluminum leads to a moderate improvement of the electrode properties; however, synthesis of the composites from molten salts and organic carbon sources allow to obtain composites, which electrochemical properties are approaching to benchtop alloy-based anode materials. Among the tested samples, Al-Gr3 composite with higher and uniform graphene content was found to be the most promising since it exhibits a low anodic polarization, so further improvement of the electrode materials by varying the synthetic approach and graphene content seems to be promising.

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