Electrical and electrochemical properties of reduced graphene oxide film for secondary battery electrode

H Aprida, S Hidayat, N Syakir, R Siregar and Fitrilawati*

Department of Physics, Faculty of Mathematics and Natural Science, Universitas Padjadjaran, Jl. Raya Bandung Sumedang km 21 Jatinangor, Sumedang, Indonesia 45363

*fitrilawati@phys.unpad.ac.id

Abstract. We prepared thin layer of reduced graphene oxide (rGO) from reduced graphene oxide powder that dispersed in deionized water and dimethylformamide (DMF) using drop-casting technique. We used carboxymethyl cellulose (CMC) as a binder in order to obtain better surface of rGO film with varied concentration of rGO. We obtained that rGO film prepared using rGO dispersed in deionized water has better surface compare to the ones dispersed in DMF. An addition of CMC into rGO has improved its film surface and increasing amount of rGO resulted higher conductivity of the sample. The cyclic voltammogram (CV) of the rGO film has shown a hysteresis curve that correspond to charging and discharging process. From CV measurement we obtain that rGO-CMC film that prepared using 3 mg/ml rGO dispersed in DI water and blend with CMC has higher specific capacitance of 400 mF/g.

1. Introduction

A battery is an electrochemical cells that consists of two electrodes i.e. anode and cathode that separated by an electrolyte [1]. It will provide a current at a voltage for a time Δt. Lithium-ion rechargeable battery has enabled a revolution of global communication.

The battery performance such capacity and cycle-ability depend on the anode material. An ideal anode material can be absorbed a large amount of lithium per-unit cell. An anode must has a good electronic and ionic conductivity as well as has a stable and reversible cycle [2]. If the anode material has a good electrical conductivity it can rapidly activate electrons and ion transport, so the charging process of battery becomes faster [3].

Graphite is a material that often used as an anode. In order to improve a battery performance, characteristics of anode materials should be upgraded. Graphene is a carbon monolayer of graphite that has 2D structure. Graphene received a lot of attention due to its excellent mechanical, electrical, thermal and optical properties. Graphene has better property compare to graphite with a thermal conductivity of 4840 W/mK - 5300 W/mK and an electrical conductivity of 2000 S/cm, which is classified as a conducting material [4].

For application, it is necessary to provide a large quantities of graphene. In relation to that, graphene oxide (GO) is mostly used as a precursor material to obtain graphene. Graphene Oxide (GO) does not have unique physical and electronic characteristics such as pure graphene properties. By eliminating or reducing the oxygen functional group will produce a structure such as pure graphene or called reduced Graphene Oxide (rGO). The oxygen group from the GO sheet can be removed by
chemical reduction, electrochemical or thermal reduction. More of oxygen functional group are reduced that showing properties increasingly similar to pure graphene, in figure 1 [5].

![Figure 1](image1.png)

**Figure 1.** Representation of sheet structure (a) Graphene Oxide (GO) and (b) reduced Graphene Oxide (rGO) [6].

In this research, we used reduced Graphene Oxide (rGO) powder with electrical conductivity ~ 667 S/m [7], thermal properties 110W/mK - 1100 W/mK at room temperature and also has an excellent mechanical resistance properties [8].

The binder material is an important part of the electrode batteries. Binder material changes the structure of rGO to binds each other. The role of binder material is related to the energy density of the active material. A good binder for ion batteries has a criteria such as having stable chemical and electrochemical properties in electrode and electrolyte systems, and also environmentally friendly [9]. One of the best binder for binding anode material is Carboxymethyl-Cellulose (CMC) [10]. The advantages of CMC are soluble in H₂O, environmentally friendly and cheaper than Polyvinylidene fluoride (PVDF) binder with using toxic N-methyl-2-pyrrolidone solvent [10]. The best properties of electrode are achieved by mixing a binder as low as possible in the active materials. An optimum concentration of CMC in active material is 2% [11]. This research intends to determine the optimum concentration of rGO in suitable solvent to analyze electrical properties to improve secondary battery performance.

### 2. Experimental

#### 2.1. Preparation of samples

We prepared thin films of rGO on Indium Tin Oxide (ITO) substrates using commercial rGO powder (Graphenea) dispersed in deionized water (DI Water) and dimethylformamide (DMF). Prior to use film preparation, the rGO was dispersed for 5 hours at room temperature using ultrasonic bath. We prepared the rGO samples mixed with carboxymethyl cellulose (CMC) as a binder with various concentration of rGO. Before mixing with rGO dispersion, CMC was dissolved with solvent and stirred for 1 hour at 60°C. The rGO-CMC mixture was dispersed for 30 minutes using ultrasonic bath. Thin films were obtained using drop-cast method and dried in the hotplate at 40°C. We prepared five type of samples as shown in table 1.

We used glass substrate (2 cm x 2 cm) for conductivity measurement and ITO or Cu foil substrate (1.25 cm x 2 cm) for cyclic voltammogram (CV) characterization. For electrolyte, we used 1M LiClO₄ solution with propylene carbonate as solvent.

| Sample | rGO (mg) | DMF (ml) | DI Water (ml) | CMC Binder (mg) |
|--------|---------|----------|---------------|-----------------|
| 1      | 1       | -        | 1             | -               |
| 2      | 1       | 1        | -             | -               |
| 3      | 1       | -        | 1             | 0.1             |
| 4      | 2       | -        | 1             | 0.1             |
| 5      | 3       | -        | 1             | 0.1             |
2.2. Characterizations
We used four-line probe method for electrical characterization and Scanning Electron Microscope (SEM) for morphology observation. The samples for SEM and conductivity measurements were deposited on glass substrate. The probe for conductivity measurement consist of four parallel line of platinum wire that connected with multimeter and DC voltage/current source. The electric current was flowed to the sample by through the probe, and the voltage was measured between two parallel probes.

Cyclic voltammetry measurement (MetrOhm Autolab) was performed using two-electrode system with platinum as counter electrode (CE), rGO sample as working electrode (WE), and 1M LiClO₄ solution as an electrolyte. Scan rate of CV measurement was varied from 25 mV/s - 150 mV/s. To study stability of the rGO-CMC electrode, we performed CV measurement on rGO-CMC sample with rGO content of 3% for many cycles at scan rate of 50 mV/s.

3. Results and discussion
Since number of oxygen functional group has reduced in rGO, it takes more time to disperse rGO powder in DI water and DMF. After dispersion rGO in DI water for a certain time with concentration up to 3 mg/ml we have a homogeneous rGO solution without aggregate. In contrast, rGO dispersed in DMF at the same concentration shows some aggregates. It was reported that rGO can be dispersed homogeneously in DMF (organic solvent) at low concentrations of <0.1 mg/ml [7]. Based on this result we only used DI water as dispersion medium of rGO.

Compare to rGO film that prepared from rGO dispersion without CMC, we found that sample prepared from rGO-CMC mixture has a better surface. An addition of CMC into rGO has improved film quality since it become more flat and homogeneous. We varied rGO content of the sample with concentration of 1 to 3 mg/ml. Surface morphology of rGO-CMC mixture with varied rGO concentration are shown in figure 2. The morphology of rGO-CMC sample is appeared similar to surface morphology of rGO sample. Amount of 0.1 mg CMC that mixed with 0.1 mg rGO seem does not change the surface morphology of the rGO film significantly. The CMC might only slight cover rGO and does not close surface of rGO layer.

Figure 2(a) is a surface morphology of rGO-CMC film prepared using rGO dispersion with concentration of 1 mg/ml and 0.1 mg CMC. The image shows that rGO-CMC film consist of a stacking of many layers of rGO with a width about 1 μm for 1 layer. Figure 2(a,2) is the same image of the sample with a magnification of 40,000 times. At the higher rGO concentration it seems the surface area get larger with a width around 3 μm, as shown in figure 2(b, c). The second image of each figure are a magnification image of 40,000x. The role of CMC as a binder is filling the voids between layers thus extending the width of the layer. The lithium ions can easily change over the electrode. With the wider surface of rGO film, lithium ions can fill the pores of the rGO layer then the electrons will be easier to move between layers.

We measured conductivity of all rGO samples including rGO sample that prepared from rGO dispersion in DI water (rGO-DI water), rGO sample dispersed in DMF (rGO-DMF) and sample rGO with CMC binder. We applied constant current from 1mA to 10 mA and measured the voltage between two probes. All measured samples show a linear I-V curve. From the I-V data, probe distance and sample dimension, the conductivity (σ) were calculated using equation (1). I in the equation (1) is the current input from DC voltage/Current Source, AV is the voltage between two probes, d is the probe distance, w is the sample wide, and t is the sample thickness. The values of conductivities of all prepared samples are shown in table 2.

\[
\sigma = \frac{I}{AV} \left( \frac{d}{wt} \right)
\]

Table 2 shows that the rGO sample prepared using DI water as dispersion medium has higher conductivity compare to the one using DMF. It is related to the quality of the resulted rGO film. Sample prepared using rGO dispersion in DMF was not flat since rGO dispersion in DMF with a concentration of 1 mg/ml has an aggregate.
Figure 2. SEM images of rGO films prepared using CMC binder with rGO concentration of (a) 1 mg/ml with magnification of 10,000x (a.1) and 40,000x (a.2), (b) 2 mg/ml with magnification of 10,000x (b.1) and 40,000x (b.2), (c) 3 mg/ml with magnification of 10,000x (c.1) and 40,000x (c.2).

An addition of CMC binder has an effect on decreasing of a conductivity of rGO since CMC is an isolator material. When the concentration of rGO was increased double or triple times, the conductivities of the rGO samples were increased significantly. The result shows that, compare to the pure rGO film, the conductivity of rGO-CMC sample does not only depend on rGO concentration, but also depend on the surface morphology of the film. The highest conductivity value of sample also related with the condition of film that has a good surface morphology with widely area. Data on table 2 shows that sample with higher rGO concentration has a higher conductivity.

Table 2. Conductivity of rGO samples with and without CMC binder.

| Samples                        | Conductivity (S/m) |
|--------------------------------|--------------------|
| rGO – DI Water 1mg/ml          | 2036.67            |
| rGO – DMF 1mg/ml               | 20.40              |
| rGO – DI Water 1mg/ml - CMC    | 671.66             |
| rGO – DI Water 2mg/ml - CMC    | 2396.38            |
| rGO – DI Water 3mg/ml - CMC    | 4188.91            |

The CV measurement were performed for all of rGO samples in LiClO4/PC electrolyte at the voltage range of -0.5 V to +1.5 V. The CV curves that measured at scan rate of 50 mV/s were shown
in figure 3. The figure shows that when the voltage applied from -0.5 V increased to +1.5 V there is an accumulation of charge between the surface of the rGO electrode and LiClO₄ electrolyte and result a current. This process is known also as charging. Then when the applied voltage was decreased from +1.5 V to -0.5 V, the resulting current response is not equal to the charging current and formed a hysteresis. This hysteresis area is described as a charge storage. The decreasing applied voltage is called as discharging process. The figure shows a comparison of CV curves of five samples. Compare to other sample, the rGO film prepared using DI water has narrowest hysteresis. While rGO film prepared using DMF has wider hysteresis compare to the one using DI water. Hysteresis area of rGO samples prepared using CMC binder are also wide enough. Its area is depended on the rGO concentration, the higher rGO concentration the wider its hysteresis area.

![Figure 3. Cyclic voltammetry curve of various rGO samples measured at scan rate of 50mV/s.](image)

From CV data that measured at varied scan rate, we calculate power of the system by using equation (2) [12]. P in the equation is a power (Watt), i is the current response in a given potential V, and the dV is step potential which was 0.00244 V. The specific capacitance C is calculated using equation (3) [12]. C in the equation is the capacitance of rGO (Farad), m is the mass of electroactive materials, ∆V is the potential window, s is the scan rate and i is the current response in a given potential V.

\[
P = \left( \int_{-0.5}^{1.5} i \, dV + \int_{1.5}^{-0.5} i \, dV \right)
\]

\[
C = \frac{1}{2m\Delta V s} \left( \int_{-0.5}^{1.5} i \, dV + \int_{1.5}^{-0.5} i \, dV \right)
\]

At the low scan rate, the lithium ions will have a longer time to get into all the pores on the electrode. Then the capacitance of rGO will be increased, but at a low of scan rate the reaction is still not stable. The value of the capacitance is likely to be declined and then stabilized along with higher scan rate value, as shown in Figure 4. Electrode with higher concentration of rGO can store more charge. The highest specific capacitance of the rGO electrode is 399.89 mF/g that achieved at scan rate of 25 mV/s using electrode contain highest concentrate of 3 mg/ml rGO prepared with DI water and CMC binder. At higher concentrations of rGO there is more charge that can be stored by electrodes.
Figure 4. Specific capacitance of rGO electrode measured at varied scan rate.

In relation to its stability, we performed CV measurement of rGO – DI Water 3mg/ml – CMC sample for 12 cycles at scan rate of 50 mV/s. Figure 5 shows hysteresis area of the sample has identical shape as a number of cycle increased. Using the measured curve and interpolation approached we obtain that the rGO-CMC electrode tends to be stable until drop capacity at 98th cycle. It provides information about a stability of the rGO – DI Water 3mg/ml – CMC electrode until 98th cycles.

Figure 5. CV curves of rGO – DI Water 3mg/ml – CMC sample after 12th cycles measured at 50 mV/s.

4. Conclusions
We obtained that rGO films prepared using deionized water and CMC as a binder has a better surface quality compare to the other ones prepared with rGO only. The rGO-CMC film that was prepared using 3 mg/ml rGO-DI water dispersion and CMC binder has a highest conductivity of 4.2 x 10⁻⁵ S/m. The cyclic voltammogram of the rGO film show a hysteresis curve that correspond to the charging and discharging characteristic of the rGO. Increasing concentration of rGO has increased number of ions can be stored in rGO film. The rGO-CMC film prepared using 3 mg/ml rGO-DI water dispersion has the specific capacitance about 400 mF/g and still has CV identical shape after 12th cycles.

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References

[1] Goodenough J B and Park K 2013 J. Am. Chem. Soc 135 1167
[2] Reddy M V, Rao G V S and Chowdari B V R 2011 Chem. Rev 113 5364
[3] Li N, Chen Z, Ren W, Li F and Cheng H-M 2012 Proc. Natl. Acad. Sci 109 17360
[4] Raccichini R, Varzi A, Passerini S and Scrosati B 2014 Nat. Mater 14 271
[5] Data Sheet: Ossila 2017 Reduced Graphene Oxide Powders
[6] Griggs C S and Medina V F 2016 McGraw Hill Encyclopedia of Science & Technology, 11th ed.
[7] Graphenea 2016 Product Datasheet Graphenea Reduced Graphene Oxide (rGO) 22
[8] Ahn H N et al 2015 Exp. Therm. Fluid Sci 60 361
[9] Qiu L et al 2014 RSC Adv 4 24859
[10] Drofenik J, Gaberscek M, Dominko R, Poulsen F W, Mogensen M, Pejovnik S and Jamnik J 2002 Sci. Direct Electrochimica Acta 48 883
[11] Hidayat S, Cahyono T, Rahayu I and Alamsyah W 2016 Prosiding Seminar Nasional Fisika p 61
[12] Chen Y, Zhang X, Zhang D, Yu P and Ma Y 2011 Carbon N. Y. 49 573