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Electrochemical Evaluation of Lithium-Ion Battery with Anode of Layer-Reduced Biocarbon and Cathode of $LiFePO_4$

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Abstract

The application of reduced carbon anode layer and $LiFePO_4$ cathode was conducted in laboratory-scale battery. Both electrodes were fabricated into lithium - ion battery with LiCl electrolyte in both gel and liquid based. The carbon was prepared by using Hummer method and solvent sonification to exfoliate the carbon layer from biocarbon. The battery performance tests were carried out in potentiostat for Cyclic Voltammetry (CV) and galvanostatic measurements. The highest current of CV measurement can be obtained in the battery with reduced carbon layer anode and 20% of liquid electrolyte. It was calculated that the same battery produced the highest energy and power. Current - Voltage profile is relatively stable in CV of batteries with 40% electrolytes in both gel and liquid media. All batteries have two peaks in both anodic and cathodic. The reduction peaks show in around 0.5 and 1.5 volts. The cathodics show in around –0.5 and –1.5 volts. The best power and energy values are given by battery with rCNSO anode and 20% liquid electrolyte. Galvanostatic profiles show that the 40% electrolytes in the batteries produces a slower discharging process. It was revealed that applying anode of layer reduced biocarbon as the battery electrode caused the discharging to run faster. The highest slope value of the galvanostatic curve can be found in the battery with the electrode of oxidized starting material and 40% of gel electrolyte, while the lowest can be found in 20% gel electrolyte with the same electrode.

Keywords

Potentiostat; Storage; Faraday; Reduction; Oxidation; Energy; Power

1 Introduction

The Lithium-ion Battery (LIB) is one of the energy storage devices. LIB is generally used in transportation, especially electric vehicles [1]. LIB can store energy due to the moving electrons from the cathode to the anode. It is illustrated that lithium ions of the electrolyte move to the interstitial structure of crystalline carbon in the anode [2].

The study has shown the relationship between high energy-power values and the morphology of carbon [3]. Biocarbon with sheet morphology has been studied in preliminary studies [4]. It was found that the thickness of sheet can be reduced by using chemical oxidation, followed by ultrasonic-assisted solvent exfoliation. Applying layer reduced biocarbon in the battery electrode has never been done before. Therefore, the information is necessary to acquire a knowledge of the relation between morphology of the carbon and electrochemical properties of the electrode [3] and performance of the battery.

The performance of the battery arises from electric current flowing from the cathode to the anode and carrying the charge [5]**.** The electrodes not only play the role as the storage for electrical charges, but also as the place where electrochemical reactions occur. The ability of the electrode to storage is affected by the morphology of carbon in the electrodes [4].

Carbon with porous and sheets morphology is one of the best anode materials LIB that has good energy and power density at intermediate cycles [6]. Carbon with sheet morphology has a high electrical conductivity [7] therefore the charge can be easily transferred through both electrodes.

Lithium ion is relatively small compared to other ions so that it easily facilitates the process of charge transfer to electrons and vice versa. Electrolyte and solvent concentrations are two factors that affect the charge transfer in the electrochemical system [8]. The charge transfer, in turn, affects the galvanostatic of battery, i.e charge discharging. Cyclic Voltammetry (CV) and galvanostatic measurements are then used to assess the

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effect of the concentrations and solvents of electrolyte on the battery performance [9].

2 Materials and Method

2.1 Carbon preparation

The starting material that was used to prepare carbon nanosheet powder was gelam wood bark which is a waste from the carpentry and wood industry. Gelam wood bark was separated from the wood and cleaned with flowing clean water and was removed from organic impurities with hot water. Gelam wood bark was milled into powder using disk mill from JIMO FF-15 and processed into carbon using hydrothermal assisted microwave pyrolysis. The procedure can be found elsewhere [10]. The process produced bio-carbon that contained carbon nanosheet (CNS). Bio-carbon was oxidized to form carbon nanosheet oxide (CNSO) by using Hummer methods. Detail explanation about Hummer method can be found in related paper [6]. CNSO was exfoliated to reduce its layer and size through sonication for 30 minutes and then heated in the electric oven at 120˚C for 2 hours to form a reduced CNSO (rCNSO).

2.2 Battery preparation

The battery was manufactured in standard assembly, i.e anode – electrolyte – cathode, pouched inside Polyethylene Terephthalate (PET) pocket. Anode preparation was carried out by mixing melamine resin and carbon nanosheet (CNS) into a paste. The 2.0 cm x 2.0 cm of paste was then used to coatthe 2.5 cm x 2.5 cm of copper plate surface using a doctor blade. The coating was calendared into two rolling rods. Coated plates were dried up in 120 ºC to produce anode for the battery. The same procedure was also applied to CNS-oxide (CNSO) and reduced CNS-oxide (rCNSO).

The cathode was the copper plate surface that was coated with $LiFePO_4$ paste. $LiFePO_4$ preparation is described in other paper [11]. Coated copper plates were also subjected to calendaring and drying steps to make cathodes. The assembly was vacuumed and sealed in an airtight pouch so that the battery is ready to be filled with electrolytes. A small hole was made on top of the PET pouch to transfer electrolyte liquid. A 20% LiCl electrolyte was injected into the battery. The injection was carried out in a glovebox and followed by hot-sealed of 200 psi load to produce battery. The same procedure is carried out for 40% of concentration for each electrolyte.

Electrolyte gel batteries were prepared by applying a polyvinyl alcohol (PVA) gel containing 20% LiCl as electrolyte. The two electrodes were aligned with the anode and cathode and formed a battery assembly. The same procedure was applied to liquid electrolyte to produce battery. Battery with a concentration of 40% electrolyte was also prepared.

2.3 Battery performance testing

The battery performance tests were carried out by using CV and galvanostatic methods. Both tests were conducted in methrohm (Autolab) potentiostat. CV is used to review the oxidation-reduction reaction pattern, current (I) and voltage (V) values. I – V profiles from the CV were used to calculate the values of energy (E) and power (P). The calculation can be seen in (1) and (2) as stated in [12].

$$P = IV \tag{1}$$

$$\mathrm{E} = \int IV\, dt \tag{2}$$

CV measurement was operated in a full-cell mode. It means that the cathode of the battery is connected to the working electrode probe of the potentiostat, inversely, the anode of the battery is connected to the reference electrode and the counter electrode probe of the potentiostat.

Charging-discharging measurement was conducted by using the galvanostat mode of the potentiostat. The battery – potentiostat connection in galvanostat mode is the same as the voltammetry measurement. In cyclic voltammetry, the potentiostat detects current production as the voltage of -3 to 3 Volts applied to the battery. Inversely, in galvanostatic mode, the potentiostat is used to measure voltage change through the discharging process as the current was changed from -2mA to 7 mA.

3 Results and Discussion

3.1 Cyclic voltammetry measurements

Three types of carbons were subjected in full cell mode in potentiostat for cyclic measurement. The measurements were performed at -3.5 volts to 3.5 volts of potential windows with 25 mV/sec of scan rate. Anodic flows take place when the scan of the potential window runs from low to high and the cathodic is the reverse scan. The existence of a peak in anodic current can be considered as reduction, inversely, oxidation in cathodic.

Figure 1 shows the CV profile of liquid and gel electrolyte of the battery. It can be shown that the highest current of CV measurement can be obtained in the battery with layer reduced carbon anode (rCNSO) and 20% of liquid electrolyte. Current - voltage profile

is relatively stable in cyclic voltammetry of batteries with 40% electrolytes both in gel and liquid media.

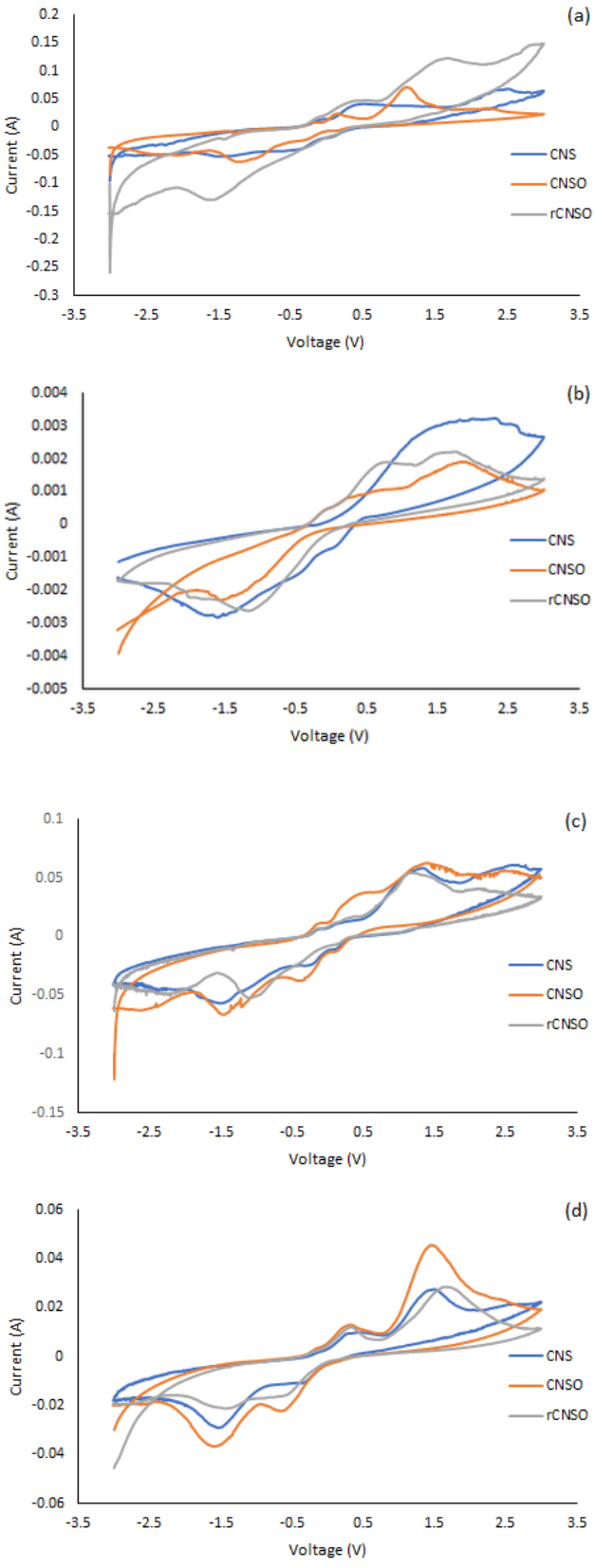

Figure 1 The CV profiles of the battery using LiCl electrolyte in various of media and concentration (%), i.e., (a) liquid 20%, (b) gel 20%, (c) 40% liquid, and (d) 40% gel.

Liquid electrolyte apparently produces higher current compared to gel electrolyte. The media affects the mobility of ions contained in lithium-ion batteries also can be found in other paper [13]. The concentrations significantly affect the CV profiles. It can be shown that higher current was built in low concentrations of liquid electrolyte, inversely, high concentration produces low currents due to the ion mobility. The charge carried by ion relatively moves freely in liquid [8]. Inversely, the visibility of the peaks on the CV profile is clearer in the gel electrolyte due to its oxidation-reduction process. Figure 1d gives clear values for where reduction – oxidation takes place. It can be seen that the batteries of all carbon types have two peaks in both anodic and cathodic. The highest reduction peak is observed in the battery with rCNSO anode and 20% liquid electrolyte (Figure 1a).

The reduction shows in around 0.5 and 1.5 volts. The cathodic shows in around –0.5 and –1.5 volts. Similar observations can be found in the paper Zhang et. al. [14]. It was interpreted that the additional peak in 0.5 and -0.5 come from the nanostructure of the carbon. Other authors report the addition of nanostructured carbon clarifies the reduction and oxidation peaks in CV profiles of lithium-ion batteries with $LiFePO_4$ cathode [15].

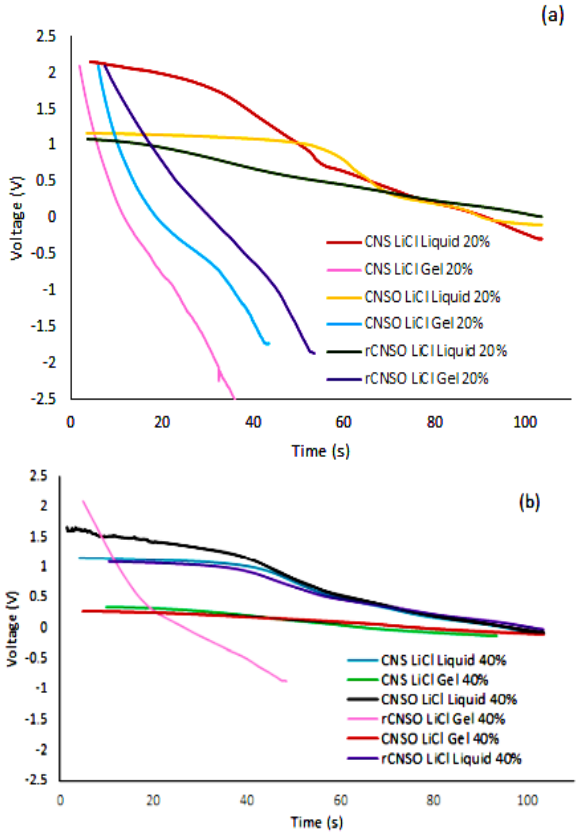

Figure 2 Galvanostatic discharging profiles of the battery using LiCl electrolyte vary in media, i.e., gel and liquid, (a) 20% and (b) 40% of concentration.

Energy and power values of the batteries were calculated by using CV profiles (voltammogram) with formula (1) and (2). The result of power – energy calculation is shown in Table 1. The best power and energy values are given by battery with rCNSO anode and 20% liquid electrolyte. It can be considered

that rCNSO has high surface area due to the reduction of the carbon layer and size. The area on the surface of carbon acts as active sites for the absorption – desorption of ions [16]. Charge storage capacity in the carbon becomes doubled after the carbon layer is exfoliated.

3.2 Galvanostatic measurements

Galvanostatic measurements were used to determine the discharging profiles and the discharging rate. Figure 2 shows the galvanostatic discharging profiles of the battery. A difference is shown in the discharging rate of the batteries according to the slope of lines (Table 1). A relatively slight slope in the CNSO electrode with 20% LiCl in gel electrolyte implies that a longer time is required in the battery discharging. Inversely, steep slope in the rCNSO electrode with 40% LiCl in liquid implies that a shorter time is required in discharging the battery. However, it is convincing to quantify the slope as shown in Table 1. The highest slope was found in CNSO with 40% gel electrolyte and the lowest can be found on CNS with 20% gel electrolyte. However, the slope value also cannot be used as a reference in this study because of the differences in the potential generated by the battery. The electric potential produced from each battery varies. The potential that was produced from the battery testing is around 0.27 - 2 Volts.

Table 1 Performance test result of the batteries

No	Variables			Parameters		
	Anode Material	**Electrolyte Type**	**Concentration (%)**	**Energy (E) (Wh)**	**Power (P) (W)**	**Discharging Slope**
1	CNS	Gel	20	1.13×10^{-8}	3.24×10^{-7}	0.129516
	CNSO	Gel	20	6.53×10^{-7}	4.82×10^{-6}	0.101847
	rCNSO	Gel	20	2.88×10^{-4}	4.21×10^{-3}	0.085949
2	CNS	Gel	40	4.23×10^{-4}	3.14×10^{-3}	0.005649
	CNSO	Gel	40	4.21×10^{-4}	3.12×10^{-3}	0.003797
	rCNSO	Gel	40	1.11×10^{-3}	8.25×10^{-3}	0.067984
3	CNS	Liquid	20	1.09×10^{-3}	1.60×10^{-2}	0.024562
	CNSO	Liquid	20	8.10×10^{-5}	6.02×10^{-4}	0.011760
	rCNSO	Liquid	20	2.27×10^{-2}	1.68×10^{-1}	0.010683
4	CNS	Liquid	40	2.92×10^{-4}	2.16×10^{-3}	0.012535
	CNSO	Liquid	40	4.43×10^{-3}	3.29×10^{-2}	0.017055
	rCNSO	Liquid	40	1.41×10^{-3}	1.04×10^{-2}	0.005509

4 Conclusion

The battery performance tests were carried out by using the cyclic voltammetry and galvanostatic methods. The highest current of CV measurement can be obtained from the battery with layer reduced carbon anode (rCNSO) and 20% of liquid electrolyte. Current - voltage profile is relatively stable in cyclic voltammetry of batteries with 40% electrolytes in both gel and liquid media. Liquid electrolyte apparently produces higher current compared to gel electrolyte. The highest slope was indicated by rCNSO with 40% gel electrolyte and the lowest can be found on CNS with 20% gel electrolyte. The reduction peaks appear at around 0.5 and 1.5 volts, while the cathodic appear at around –0.5 and –1.5 volts. The best power and energy values are given by battery with rCNSO anode and 20% liquid electrolyte. Galvanostatic profiles exhibit that the 40% electrolytes in the batteries produce a slower discharging process. It was revealed that applying anode of layer reduced biocarbon as the battery electrode caused the discharging to run faster. The highest slope value of the galvanostatic curve can be found in the battery with the electrode of oxidized starting material and 40% of gel electrolyte, while the lowest can be found on a 20% gel electrolyte with the same electrode. The method that was applied during the preparation of materials and batteries shows good results with high power-energy values. It can be proposed to use carbon materials in capacitor and battery manufacture.

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