Synthesis and characterization of carboxymethyl cellulose (CMC) from salak-fruit seeds as anode binder for lithium-ion battery

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Abstract. Lithium-ion batteries are most popular battery for applications as portable electrical energy storage. Lithium-ion battery have some advantages compared to other battery such as have large specific energy capacity, light weight and long-life span. One of the components that contribute to the quality of Lithium-ion batteries is the binder material. Carboxymethyl Cellulose (CMC) is one of the most widely used binder materials other than PVDF. CMC can be synthesized from various organic materials such as empty bunches of palm, water hyacinth and salak-fruit seed. In this research, CMC is obtained from waste of salak-fruit seed (Salacca zalacca) and then used as anode binder in lithium-ion battery. The steps of CMC synthesis consist of cellulose isolation from salak-fruit seed, followed by alkalization process, carboxymethylation and finally the purification process. FTIR spectrum of CMC shows the successfully of CMC synthesis, the presence of strong absorption band at 1600 cm-1 and 1438 cm-1 is related to stretching vibration from the carboxyl group (COO-) and carboxyl group as it salts (COO-Na), respectively. The absorption in the region 1321–1400 cm-1 is due to symmetrical deformations of CH2 groups while broad absorption at around 3400 cm-1 is due to the stretching of the hydroxyl groups (-OH). Application CMC as binder of graphite anode with 5wt% CMC shows good surface profile and evenly distributed cavities with conductivity of about 0.815 S/cm.

1. Introduction

Lithium-ion battery (Li-ion) has been known as the best electrochemical devices for electrical energy storage. Li-ion battery has high energy density, long life cycle (500-1000 cycles), light weight and environmentally friendly [1]. Energy density of the battery during charging or discharging process depends on its active material. The active material of Li-ion battery plays an important role on the intercalation of Li+ ion from anode to cathode and vice versa. The active material needs a binder in order to keep the compactness and a high particle density of electrode. On the other hand, existence of binder material will affect the stability and loss capacity of the battery. If binder material is poor, then the loss energy of battery will increase and cause battery damaged [2].

Generally, polyvinylidene fluoride (PVDF) was used as binder in the cathode and anode of commercial Li-ion batteries. PVDF has good electrochemical stability and act as a good adhesive for the active material on the substrate. However, PVDF have some disadvantages, i.e.: expensive, not easy to recycle and involved the use of volatile organic compounds for its processing such as such N-
methyl-2-pyrrolidone (NMP) which a harmful and toxic solvent [3]. The use of water-based binders has been done by Lestrie et al. 2007 [3]. Water-based binders also simplify the process of making the battery electrodes. One of the most used water-based binder materials is Carboxymethyl cellulose (CMC).

CMC is a cellulose derivative that is widely used in many industries such as food, pharmaceutical, detergent, textile and cosmetic products. CMC is mostly used as thickeners, emulsion or suspension stabilizers and binders. CMC can be made from plants therefore it can be readily available in large quantities as well as it is renewable. Initially CMC was mostly made of wood cellulose because of its sufficient cellulose content, which is about 42-47%. However, many CMC today is developed from non-wood materials such as stem and empty bunches of palm oil, bananas, water hyacinth plants and salak-fruit seeds.

Salak-fruit seeds are waste from the salak-fruit and they are abundant in Indonesia. The research of salak-fruit seeds showed that salak-fruit seeds contained about 35% of cellulose [4]. Cellulose can be processed into derivatives such as CMC (Carboxy Methyl Cellulose), MC (Methyl Cellulose), HPC (Hydroxy Propyl Cellulose), and HPMC (Hydroxy Propyl Methyl Cellulose). The CMC is a linear cellulose polymer with an anion compound which properties are biodegradable, colorless, odorless, non-toxic, soluble in water (powder form), pH range of 6.5 to 8.0, transparent and un-reacting with organic compounds. The chemical structure of CMC is showed in figure 1.

![Figure 1. Chemical structure of CMC.](image)

The solubility of CMC in water can be changed by controlling the amount of carboxymethyl sodium compounds that are substituted into the CMC chain. The amount of the hydroxyl group that substituted by the sodium carboxymethyl group is called as the substitution degree. Increasing the substitution degree will increase the solubility of CMC in the water [5]. High solubility of CMC will increase the electrode surface area and improves the efficiency of ion exchange between the electrode and electrolyte, furthermore will increasing capacity of battery.

**2. Method**

Several materials were used in obtaining CMC from salak-fruit seed, such as NaClO₂, NaOH, sodium monochloaoetic (NaMCA), CH₂COOH, ethanol and distilled water. Firstly, Salak seeds are separated from the fruit and then crushed into powder, and sieved through 100 mesh. Furthermore, the powder was heated at 110°C in the oven for about 2 hours. The second step is the isolation process of cellulose that consists of de-hemicellulose and bleaching. The step of de-hemicellulose was conducted by dissolving salak-seed powder in 17.5% NaOH for about 3 hours. The next step is removing lignin or bleaching process which conducted by dispersing powder precipitate from previous process in 1 wt% NaClO₂ [6].

Alkalization process started by adding the cellulose powder into solvent of isopropanol and ethanol, with volume ratio of 80:20, and stirred using magnetic stirrer for about 15 minutes. Then, 30% NaOH (w/v) was added dropwise into the mixture and was stirred for 1 hour at 30°C. The final step is carboxymethylation process which was done by adding sodium monochloaoetic (NaMCA) dropwise. Prior to use, NaMCA was dissolved in water and isopropanol. The carboxymethylation process was carried out at 55°C for about 4 hours. The solution was then cooled to room temperature and the slurry was filtered. The slurry was filtered and then dissolved in 70% of ethanol. The solution was neutralized using 98% acetic acid. After it was filtered and washed using 70% ethanol to remove undesirable reactants, the product was dried at 70°C for 5 hours [6]. The final product of CMC was in the powder form.
The produced CMC was analysed using FTIR to characterize its molecular structure and test its purity. Moreover, the characterization was also carried out to anode layer of CMC-graphite-C on the glass substrate. The characterization consists of conductivity measurement and surface profile imaging using Scanning Electron Microscopy (SEM). These characterizations are carried out to investigate the quality of CMC in its application as binder in the battery electrode.

3. Results and Discussion
Figure 2 shows the FTIR spectrum of CMC powder. The peaks of absorption are related to vibration frequency of the chemical bonds in the CMC compound. The presence of the absorption peak at 1600 cm$^{-1}$ corresponds to stretching vibration of the carboxyl compound (COO-) while the absorption peak at 1438 cm$^{-1}$ corresponds to streaking vibration of the carboxyl compound in the form of salt (COO-Na). In the fingerprint region, strong absorption occurs in the wide range of 950-1250 cm$^{-1}$, this shows the presence of ether bonds in the CMC compound. In addition, the absorption bands at 1321 cm$^{-1}$ corresponds to symmetrical deformation of CH$_2$ molecule, and presence of broad bands absorption at 3400 cm$^{-1}$ corresponds to stretching frequency of hydroxyl molecules (-OH).

![FTIR spectrums of CMC from salak-fruit seed.](image)

Purity test of CMC was carried out by titrating the CMC solution using AgNO$_3$ and K$_2$CrO$_4$ as indicator. The purity of CMC can be calculated using equation (1) and (2) [7].

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Purity \text{ of CMC} = 100\% - \% \text{NaCl}
\]

\[
\% \text{NaCl} = \frac{V \times N \times 58.45 \times 100\%}{A \times (100 - B)}
\]

where $V$ is Volume of AgNO$_3$ (ml), $N$: Normality of AgNO$_3$ (0,1N), $A$: mass of CMC (500 mg) and $B$: water content of CMC (%). Based on the purity test, within three samples tested (CMC mesh-100, CMC mesh-60 and CMC, mesh-40), the results are 94%, 93% and 93%, respectively. These results prove that CMS has actually been formed with high enough purity.

Figure 3 shows the SEM images of CMC-graphite-C composites with different concentration of CMC. All samples show some slab which are connected to each other. Morphology of CMC-graphite-C layer is observed as flaky texture reflecting the graphite particle wrapped by CMC layer as shown in figure 3 for all concentration at magnification 1000x. The larger interspaces of the layer and the thinner layer edges of CMC-graphite-C can be clearly seen in figure 3 with magnification 5000x. The material composites show many cavities, which may be formed during the stirring in aqueous media and drying process. The composition of 1% CMC shows too many cavities and uneven distribution of CMC. Furthermore, the composition of 5% CMC shows good surface profile with evenly distributed cavities, while the composition of 10% CMC shows homogenous surface profile but too much CMC that will effect in too low conductivity.
Figure 3. SEM images of CMC-graphite-C layer (a) 1wt% CMC, (b) 5wt% CMC, (c) 10wt% CMC.

Figure 4 shows the conductivity measurement which was carried out by four-line probe method. The measurement was performed for different concentration of CMC started from 2% to 10%. Generally, the addition of CMC powder into graphite-C layer can increase the mechanical properties, but reduce its conductivity. The optimal composition of CMC in the CMC-graphite-C composite is 5% CMC which has the highest conductivity of 0.815 S/cm. This result is correlated with the SEM image where the composition of 5% CMC has good surface profile with evenly cavities distribution.

Figure 4. Conductivity of CMC-graphite-C layer with various composition of CMC.

4. Conclusions
Carboxymethyl cellulose (CMC) can be extracted from salak-fruit seed with high purity up to 94%. The analysis results of FTIR spectrum shows that molecular structure of CMC synthesized from salak-fruit seed has been formed. Based on SEM image, the CMC-graphite-C layer shows some slab which are connected to each other with cavities distribution. The addition of CMC into graphite layer can increase the mechanical properties, but reduce its conductivity. The optimum composition of CMC-graphite-C is 5:85:10, which has good surface profile with evenly distributed cavities, and has the highest conductivity 0.815 S/cm.
Acknowledgments
The authors would like to thank to Riset Kompetensi Dosen UNPAD (RKDU) Project 2017 for financial support.

References
[1] Hamid N A, Wennig S, Hardt S, Heinzel A, Schulz C and Wiggers H 2012 J. Power Sources 216 76
[2] Nitta N, Wu F, Lee J T and Yushin G 2015 Mater. Today 18 252
[3] Lestrie B, Bahri S, Sandu, Roué L and Guyomard D 2007 Electrochem. Commun. 9 2801
[4] Anggrahini S, Marseno D. W, Setiyoko A and Wahyuningtyas A 2017 Indonesian Food and Nutrition Progress 14 101
[5] Haleem N, Arshad M, Shahid M and Tahir M A 2014 Carbohydr. Polym. 113 249
[6] Hidayat S, Susanty, Riveli N, Suroto B, Rahayu I 2018 AIP Conf. Proc. 1917 030023-1
[7] Saputra A H, Qadhayna L and Pitaloka A B 2014 Int. J. Chem. Eng. Appl. 5 36