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Best Formulation of Water-Based Slurry Making for Excellent Lithium Nickel Cobalt Aluminum Oxide ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) Performance

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ABSTRACT: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) is one of Ni-rich in Li-ion battery cathode family that offers capacity around 200 mAh/g high energy density, low cost, non-toxicity, and superior thermal stability. To produce some good performance of the batteries, it's needed the best slurry which is prepared for coating process making in water-based system. Due to remarkably improved the bonding capacity, cycle stability, rate performance of battery cathode. The formula of Lithium Nickel Cobalt Aluminum Oxide ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ or NCA): Acetylene Black (AB): Carboxymethyl Cellulose (CMC): Styrene Butadiene Rubber (SBR) is has many ratios as 80:10:5:5, 80:10:3:7, 90:6:2:2, 90:5:2:3, 85:10:2:3, and 80:15:2:3. All of formula can stick on Al-foil, so the electrode sheet can make by aqueous-based system but should be have appropriately formula and some of slurry not enough to coat on Al-foil because it has less slurry. Summary all of cathode sheet has voltage 3.7 V. The formula has the capacity/gram around 121.1-132.8 mAh/g and efficiency around 85%-97%, Formula 4 (90:5:2:3) is best formula has high capacity when compare with another formula and after calculate that has capacity/gram 132.8 mAh/g and high efficiency 95-97%.

Keywords: NCA, Slurry, Coating, Water-based, Electrochemical

1. Introduction

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode has found relatively widespread commercial using of Lithium-Ion batteries, for example, in Panasonic batteries for Tesla Electric Vehicles. NCA has high usable discharge capacity around 200 mAh/g and long storage calendar life compared to conventional Co-based oxide cathode. NCA cathode material is one of Ni-rich in Li-ion battery cathode family that offers high energy density, low cost, non-toxicity, and superior thermal stability [1], [2]. Beside of NCA advantages, Ni-rich cathode such as NCA now is facing a challenges from LFP which has discharge capacity 165 mAh/g and cobalt-free cathode where electrochemically stable for developing high energy of Ni-rich cathodes [2], [3].

There are common processes for making Li-ion battery such as synthesizing the cathode and anode material, coating process, battery assembly, battery performance test, and packaging. Coating process is mainly important which gives the big impact for the battery product [4]. To produce some good performance of the batteries, it's needed the best slurry which is prepared for coating process [5]. The electrode slurry consists of active material, conductive agent (Acetylene Black), and binder [6]. The attractive forces by the binder and active material provided connectivity to the slurry system, thus generating a network structure for electrodes [7]. The slurry preparation can be divided as two systems based on the using of binder. There are a water-based (aqueous) system using Carboxymethyl Cellulose (CMC) combined with Styrene Butadiene Rubber (SBR) and an organic solvent-based (non-aqueous) system using Polyvinylidene Fluoride (PVDF) blended with N-methyl-2-pyrrolidone (NMP) [8], [9].

Water-based system provides some advantages such as it has environmental consistency, low-cost consideration, remarkably improved the bonding capacity, cycle stability, rate performance of battery cathode, and it was suitable for making transition metal oxides cathode of Li-ion battery, better than organic solvent-based. Meanwhile, PVDF binder is insufficient to cope with high-potential operations and large volume change during lithium insertion or extraction, and the adhesion strength of the composite layer onto a current collector is not enough to avoid material detachment. Beside of this, NMP as the solvent of PVDF is so harmful and combustible [10], [11].

For another background, SBR provides not only good binding for electrode powders but also the required adhesion of electrode sheets to the current collector. SBR comes in the form of an aqueous emulsion, which has very low viscosity and does not facilitate the wetting of its fabricated electrode slurry on the current collector during casting and were obtained from emulsion polymerization [12], [13].

To improve the wetting, SBR is generally blended with the thickening agent, CMC [14]. Beside of this, CMC binder become extremely stiff and brittle after vacuum drying, but after blending SBR and CMC results in electrodes that are less brittle and then show the improved physical properties [15]. CMC is synthesized from cellulose with a simple alkali-catalyzed reaction to disturb strong intra-molecules hydrogen bonds with carboxyl groups along the polymer chain so that give good water solubility [9]. Beside of this, the reason of adding CMC has forever been considered as an economic, biodegradable, and also thermally stable natural polymer [16]. However, the using of many SBR can make the electrode sheet has pores and if use many CMC can make the slurry has high viscosity that reasons have some limitation effects on result of batteries performances, such as poor electron conductivity and decreased electrolyte permeability [8]. Because of that, it should be careful about ratios of CMC and SBR adding.

This study is purposed to investigate how the cathode slurry can stick on the aluminum foil and increasing durability of Li-ion battery based on battery testing system. For doing this research, the formula of water-based slurry cathode material is manipulated to find the best compositions in coating slurry for production Li-ion battery especially for NCA cathode material.

2. Experimental Method

2.1 Material

The main materials in this research consists of NCA cathode material, Acetylene Black (AB) (MTI Corporation) as conductive agent, Carboxymethyl Cellulose (CMC) (MTI Corporation) as dispersant, Styrene Butadiene Rubber (SBR) (MTI Corporation) as binder compound, and water as dispersion media [17]. All the materials are required to earn the best slurry for NCA coating process.

2.2 Methodology

This research runs out based on Figure 1. below. There are some steps to produce Li-ion battery with NCA cathode material. The first is slurry preparation and manufacturing which is purposed to make the homogenous slurry materials. Basically, the slurry manufacturing is a complex process with multiple steps, active materials, conductive agent, and binders are mixed into a slurry, then coated onto a metallic current collector and dried. The next step is positive electrode manufacturing and battery assembly i.e. calendaring, electrode slitting, winding, welding, and electrolyte filling [4]. Then, the final step is battery testing for knowing the capacity and cycles of battery to interpret the durability and lifetime.

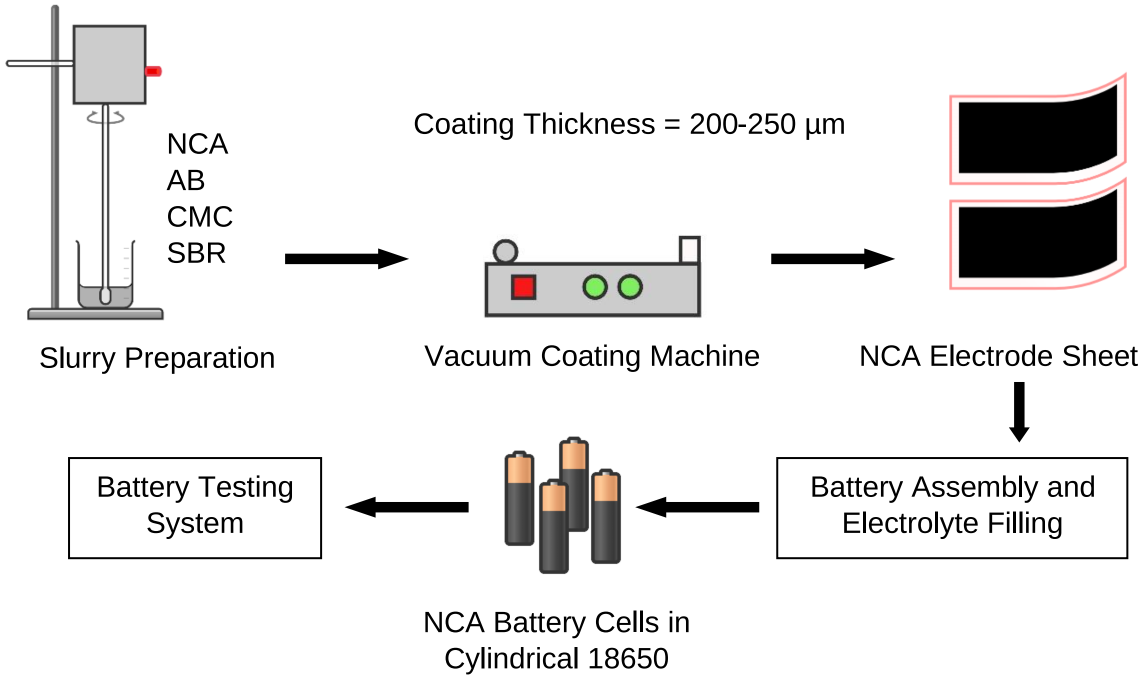

Figure 1. Schematic Diagram of Water-Based Slurry Production to Li-Ion Battery Cells

2.2.1 Cathode Slurry Manufacturing

Slurry preparation started by set the apparatus (Figure 1.) and add the CMC (MTI Corporation) into a half of the total water requirement and it is mixing for an hour. Due to CMC is thickening agent, if the adding of CMC after added other materials will make the slurry can't disperse and mix together. The second addition is NCA cathode materials powder with 200 mesh in particles size and Acetylene Black (AB) (MTI Corporation), then continue the mixing for 2 hours until become slurry-textured. After that, add the SBR into the slurry for blending the all materials. After the slurry mixing finished, the cathode slurry could have screening to make sure it blends thoroughly because if agglomerates remain in the slurry, they can later lead to a faster capacity fading of the battery cell [5].

The main variable of this research is the ratios formula in mass fraction (%) about cathode active materials, AB, CMC, and SBR that giving a big impact on the electrochemical cell performance. There are some compositions of the cathode slurry for coating process represented by Table 1. below. For the amount of water which is added in this slurry making method, it counted 115% from total cathode active material following Eq. 1 to reach the best viscosity.

$$\text{Total water} = 1.15\% \times \text{total cathode active material (gram)} \quad (1)$$

Table 1. Ratios Formula of NCA: AB: CMC: SBR in Mass Fraction

Formula	Ratios			
	%NCA	%AB	%CMC	%SBR
1	80	10	5	5
2	80	10	3	7
3	90	6	2	2
4	90	5	2	3

2.2.2 Coating, Battery Assembly, and Battery Testing

The fine slurry coated on aluminum foil as current collector with coating vacuum machine by specifying the thickness of slurry around 200-250 μm. The thickness lies in the range between 40-300 μm commonly [18]. After the first side of the positive electrode sheet bring a cathode electrode sheet to oven with temperature around 170-200 °C and bring the positive electrode sheet out for doing another side like the first side. At last, put a dry cathode electrode sheet in a vacuum oven around 30 minutes before doing battery assembly.

Battery assembly runs in some processes. The first step is pressing or calendaring cathode electrode sheet with pressing machine and slit the cathode electrode sheet into 5.6 cm width and 25 cm the length with slitting machine. Then, aluminum strip as positive pole is welded on the cathode electrode sheet with ultrasonic welding machine and stick the electric tape on top of cathode electrode sheet by cover aluminum strip. It purposed to avoid electrical short. After that, the cathode electrode sheet with separator and anode electrode sheet are winded using winding machine. For the anode electrode, actually made from graphite. Next step, spot welding machine is operated to weld the Ni-electrode stick from the anode sheet to cylinder 18650 cell case. Cylinder cells have grooved with semi-auto grooving machine and welded the aluminum strip on the positive electrode to anti-explosive cap and insulation O-ring. Bring the cylinder cells into glove box for dropping 5 mL electrolyte $LiPF_6$ to earn good thermal stability, electrochemical performance, and transport ion properties [19], and close the cap before bring the cylinder cell out. Sealing cylinder cells with sealing machine. After the batteries are ready, they run into battery testing system to measure off the capacity and cycles. Then, we need to calculate 1C from mass of cathode material like Eq. 2 below and for knowing the capacity/gram of the cells result, it calculated following Eq.3.

$$1\text{C} = \text{mass of cathode} \times \frac{\%\text{ of formula}}{100} \times 200 \text{ (theoritical capacity of NCA)} \quad (2)$$

$$\text{Capacity/gram} = \frac{\text{Discharge Capacity}}{1\text{C}} \times 200 \text{ (theoritical capacity of NCA)} \quad (3)$$

3. Results and Discussion

Based on this research, SBR and CMC are the main components in water-based slurry system. CMC is used as thickening agent and anti-precipitant when preparing electrode of Li- ion battery [20]. Meanwhile, SBR is aqueous based binder which is mainly used to prepare electrode for Li-ion batteries. Such binder is characterized by strong adhesion and high aging-retardant [8]. There are four formulas that show the different ratio about CMC and SBR. Formula 1 (NCA: AB: CMC: SBR = 80:10:5:5) has high viscosity cause as many CMC. Meanwhile, the electrode sheet of formula 2 has bubble cause after screen slurry has spin and has pores because used many SBR. Then, the electrode sheet of formula 3 has crack and don't cover all and not enough for 2 sides cause less slurry. For the best result in physical and visual, formula 4 produced electrode sheet with no cracks and pores. In Addition, all slurries of the formula can stick on the aluminum foil.

The pores that found on cathode sheet especially in formula 3 can conduce the down of electrochemical performance. Its caused by bubble can expose aluminum foil as the current collector which give direct contact with electrolyte [21]. The defect of electrode sheet such as having crack for formula 3 is caused by agglomerates from binder and acetylene black. The agglomerates can lead to higher inactive components and lower the cell capacity [21].

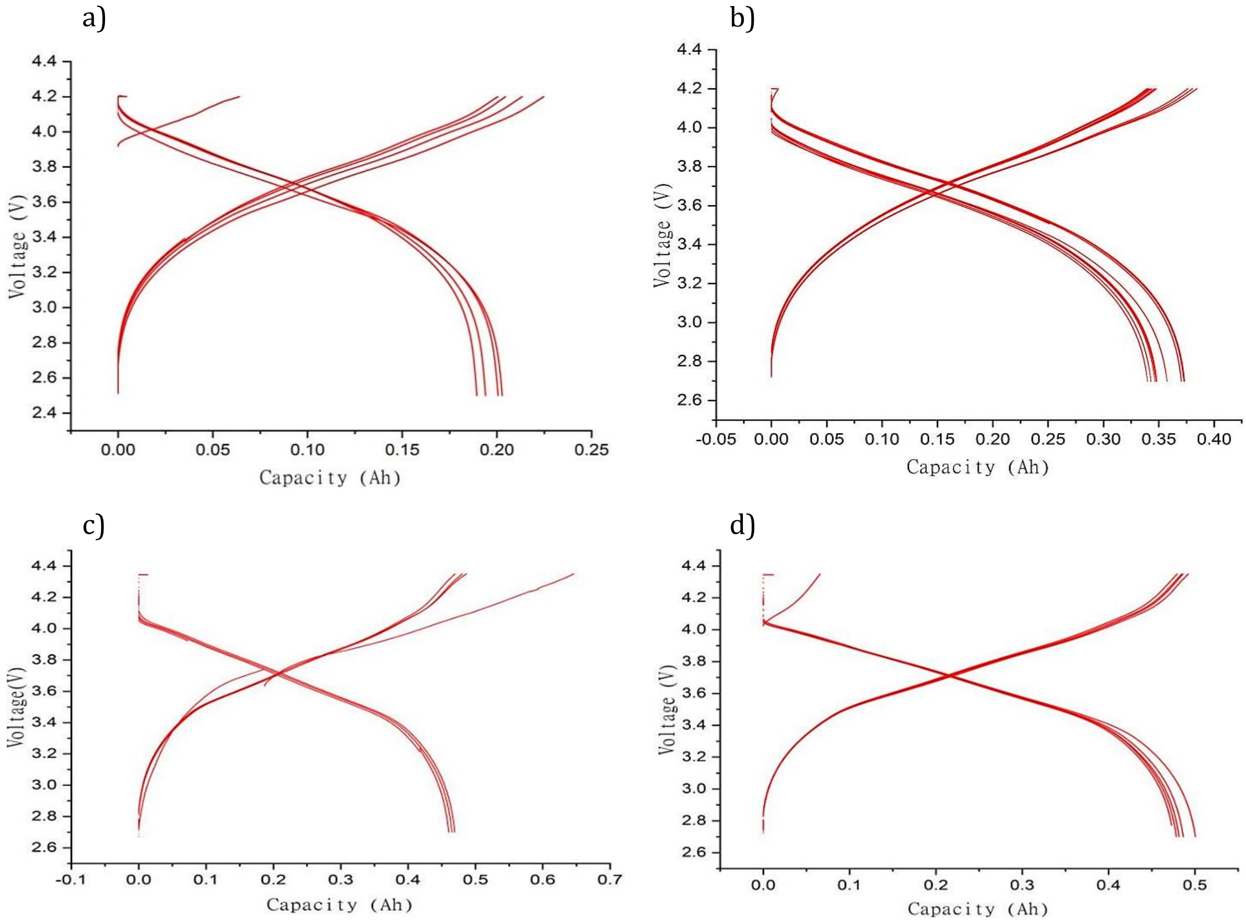

Figure 2. Capacity (Charge-Discharge) Data of the Cells in Each Formulation: a) Formula 1; b) Formula 2; c) Formula 3; d) Formula 4

Based on the Figure 2., there are capacity data in each formula that give some important points. the result of formula 1 has capacity charge 226.87 Ah, capacity discharge 200.64 Ah, efficiency 90 %, and capacity 128.86 mAh/g. Formula 2 earn capacity charge 438 Ah, capacity discharge 373 Ah, efficiency 85%, and capacity/gram is 125.67 mAh/g. Formula 3 runs in capacity charge 496.3 Ah, capacity discharge 465.0 Ah, efficiency 93-95%, capacity/gram is 121.2 mAh/g. For the best result in this study, there is formula 4 which perform capacity charge 546.8 Ah, capacity discharge 519.9 Ah, efficiency 95-97%, and capacity/gram is 132.8 mAh/g.

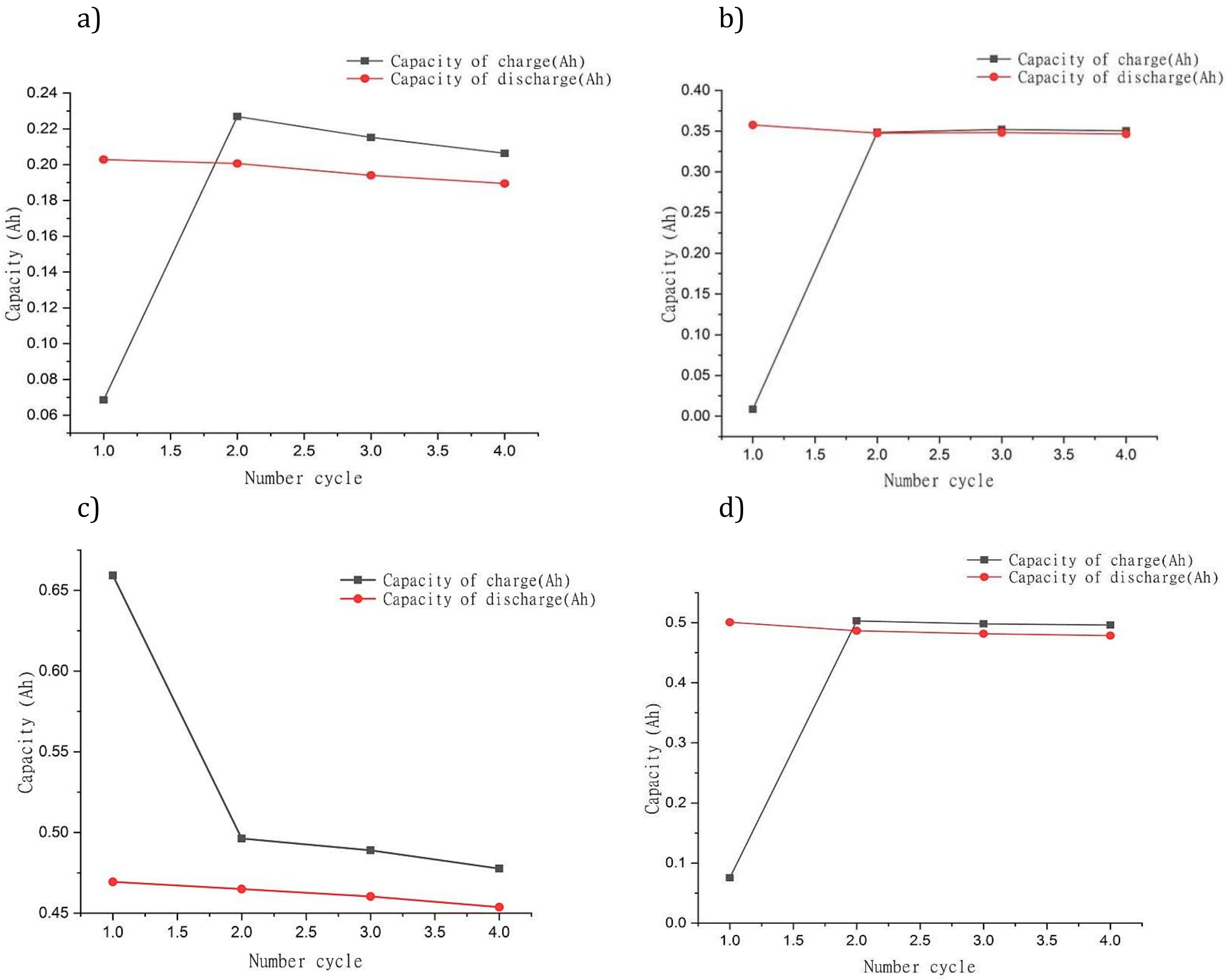

Figure 3. Cycles of the Batteries in Each Formulation: a) Formula 1; b) Formula 2; c) Formula 3; d) Formula 4

Figure 3. show the cycles of the cells that formula 1, 2, and 4 similar in trends. The first cycle has low capacity of charge because at first time the cylinder cell has charge before measure by battery analyzer machine. Meanwhile the cycle of formula 3 perform the first cycle has high capacity of charge but low capacity of discharge and next cycle has constant than. About cycle data, formula 2 and 4 give the charge-discharge capacity which is squeezed in 3 last cycles. It concludes that formula 2 and 4 are the best in cycles data among the others.

4. Conclusion

The formula of Lithium Nickel Cobalt Aluminum Oxide ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ or NCA): Acetylene Black (AB): Carboxymethyl Cellulose (CMC): Styrene Butadiene Rubber (SBR) is has many ratios as 80:10:5:5, 80:10:3:7, 90:6:2:2, 90:5:2:3, 85:10:2:3, and 80:15:2:3. All of formula can stick on Al-foil, so the electrode sheet can make by aqueous-based system but should be have appropriately formula and some of slurry not enough to coat on Al-foil because it has less slurry. Amount of CMC and SBR has be important, if the slurry has high CMC it will hard to blends and the slurry has high viscosity or the slurry has high SBR can make the cathode sheet has many pores because SBR is rubber. Summary all of cathode sheet has voltage 3.7 V. The formula has the capacity/gram around 121.1-132.8 mAh/g and efficiency around 85%-97%, Formula 4 (**90:5:2:3**) is best formula has high capacity when compare with another formula based on Figure 4. and after calculate that has capacity/gram 132.8 mAh/g and high efficiency 95-97%.

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Author Contributions

Miftakhul Hakam, Afifah Nur Chairinnisa, and Rheina Jelita Adristy carried out the experiment and wrote the manuscript with a helpful support from Tika Paramitha as supervisor of the overall project. The final report was committed by all contributors.

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