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Solid Polymer Electrolyte (SPE) from Corn Starch and Aluminum Nitrate Salt Composites for Aluminum - Ion Battery

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Abstract. The increasing of need for portable electrical energy makes the demand for rechargeable batteries high. Aluminum-ion battery with Solid Polymer Electrolyte (SPE) produced from the natural polymer corn starch with salt additive has the potential to be developed. The flexibility and resilience of SPE are enhanced by glycerol ($C_3H_8O_3$). Throughing gelatinization of the linear monomer chains to become amorphous, the space for the ions in it is more free so that the ionic conductivity is high. By means of solution casting, heating temperature of 50ºC for 9 hours found SPE with a strong structure. With the same concentration CS-Al has a higher conductivity with $\sigma = 4.93 \times 10^{-5}$ S/cm than CS-Na whose value is $\sigma = 2{,}92 \times 10^{-5}$ S/cm. This is due to the SPE CS-Al show more amorphous structure which allow more flexible ionic segmental motion. This is in accordance with XRD resulting which shows that the addition of aluminum nitrate salt is more amorphous than sodium acetate; the shift in peak pattern is also greater due to cation intercalation Al^{3+} with corn starch. FTIR is the result found that nitrate fixed by corn starch, indicated a change in the hydroxyl group of corn starch amylopectin. SEM photo of result also showed aluminum nitrate salt ion more easily in overcoming than sodium acetate. The indicate of SPE was more homogeneous because corn starch was already intercalated. They are combined to Al^{3+} and NO_3^- ions. With this value it can be an appropriate reference for developing SPE on Aluminum-ion batteries with aluminum nitrate salts have higher performance and environment friendly.

1. Introduction

The development of the battery is started from a primary battery (non-rechargeable) with a small ability to store electrical energy and then developed into a secondary battery (rechargeable). Currently, the most of the secondary batteries on the market are based on lithium ion. This happens because lithium-based batteries can store and provide considerable energy and also power [1]. In addition, lithium metal has electropositive properties, thus providing a high energy density [2]. In fact, the abundance of lithium in nature is very limited, and the waste lithium-ion batteries are included in B3 (Toxic and Hazardous Materials) waste [3]. So, there is an urgent needs to find alternative battery technologies that it can be ballance costs and performance with environment friendly .

Aluminum is a metal with a fairly high abundance in the earth's crust (82,000 ppm), has a gravimetric energy density of 2980 $mAhg^{-1}$ and volumetric capacity 8046 mAh cm^{-3}, 4 times higher than Li (2062 mAh cm^{-3}) [4] so that aluminum is an ideal element for rechargeable batteries [5]. The differentiate with the lithium, there are other metals such as sodium [6], potassium [7], magnesium

[8] and aluminum [9]. It can be used for reversible intercalation or deintercalation processes. The differentiate between to sodium and potassium, aluminum has a smaller ion size, higher theoretical capacity and is less reactive, making it easier to handle. [10].

Starch is a renewable, inexpensive polysaccharide polymer, and contains a lot of –OH chemical particles so that it is open to the possibility of modification and the ability to melt processes in the presence of plasticizers [11]. The Corn starch which consists of long chains of starch molecules and when heated in a dissolved state will cause the solution to thicken. This condition is due to the reaction of water absorption or the gelatinize process into corn starch. This starch has many advantages over synthetic plastics which are generally single-use applications with superior mechanical and electrical characteristics [12], It can be produced at low cost, there are abundant and renewable raw materials with good biocompatibility [13] [14] [15]. In addition, other properties of corn starch are solubility and high recrystallization stability from the amorphous phase [16].

The most natural polymers are such as starch exhibit relatively low ionic conductivity [17]. To increase the conductivity, several attempts have been made such as by mixing the polymer to produce 1.5×10^{-4} S cm^{-1} [18], plasticization to produce 3.86×10^{-3} S cm^{-1} [19], the addition of ceramics produced $(1.99 \pm 0.02) \times 10^{-4}$ S cm^{-1} [20] and the addition of NaCl salt resulted $(1.72 \pm 0.12) \times 10^{-5}$ S cm^{-1} [21]. Based on the research results, the concentration and type of salt also affect the ionic conductivity of the polymer. The higher is the salt concentration, the lower the degree of dissociation [22].

The relationship between aluminum and corn starch to be used as a battery making material is that the aluminum as an ion-producing metal with a hollow structure, while corn starch using as a space holder or as a polymer matrix whose ionic conductivity can be increased by adding salt. By being formed as a positive and negative electrode of aluminum metal, ionic conductivity will occur between the two poles when connected to a conductive polymer material so that a rechargeable battery system can be produced [10]. Conditioning the polymer electrolyte in the solid state is the right choice compared to the liquid or gel form. This is because in the solid state of the material in addition to its main properties of high ionic conductivity, other desirable properties are to have good electrochemical stability, flexibility, leakage free so that it is safe to use, and has a long life cycle [23].

2. Research Description

2.1 SPE Synthesis

Making SPE by solution casting, aluminum nitrate ($Al(NO_3)_3$) is put in 50 ml of H_2O in a beaker while stirring at 1200 rpm for 15 minutes to dissolve optimally, then 1.75 ml of 85% glycerol or 2.198 grams and 2.5 grams of corn starch were added. This process was continued while the solution and it is still stirred, 10 minutes later the beaker in covering with plastic wrap and put in a water bath and hot plate magnetic stirrer with a temperature of 90°C and 1200 rpm for 1 hour until homogeneous. The liquid was removed to be cooled while being stirred again for 10 minutes and poured into a petri dish. Furthermore, it is evaporated to increase the viscosity of the solution by placing it in an oven at 50°C for 9 hours until the liquid forms a solid so that SPE sheets are produced from corn starch. Show in Figure 1.

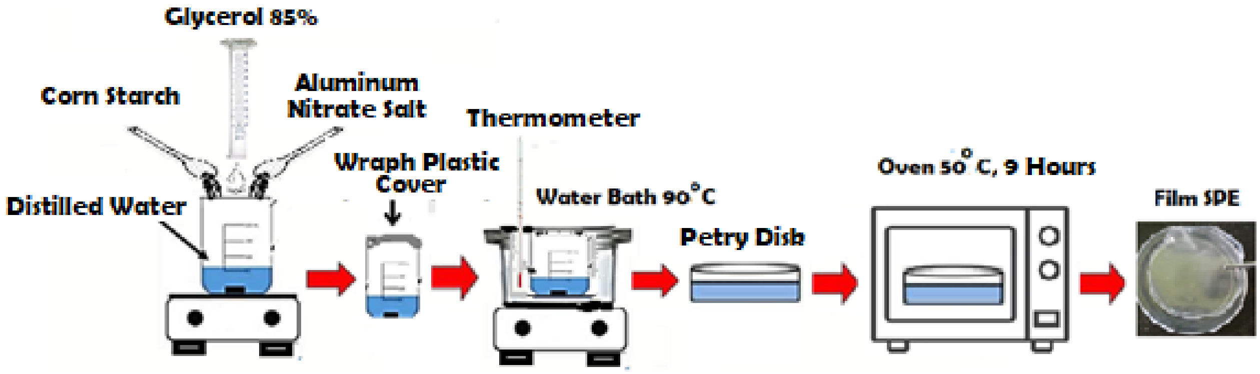

Fig. 1. SPE synthesis process of SPE in the laboratory

This process is also for sodium acetate salt (CH_3COONa), accordance with research that has been carried out the optimal concentration for sodium-based SPE is at 15% [24]. So in this research were 3 test samples, SPE 0% of cornstarch without salt (CS) as baseline, SPE 15% aluminum nitrate (CS-Al) and SPE 15% sodium acetate (CS-Na).

The use of aluminum nitrate salt SPE material in the aluminum-ion battery system is according to the following scheme in Figure 2

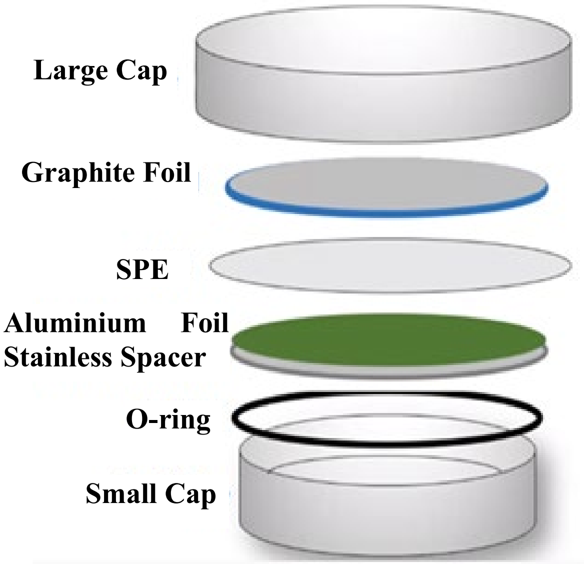

Fig. 2. SPE Coin cell design for Aluminum-ion Battery

The cathode contains aluminum foil because it is ionically and electrically conductive. The anode negative electrode is used graphite foil, because it is able to store and release ion charges well, has a long usage cycle rate, is easy to process, and safe to use. SPE as a solid electrolyte besides functioning as a conductor of aluminum ions from the anode to the cathode and on the contrary with its solid form also functions as a separator to prevent short circuits and contacts between the cathode and anode. This SPE separator is ionic conductive but not electrical conductive.

2.2 Characterization of SPE Materials

Electrochemical Impedance Spectroscopy (EIS) was chosen over the Four Point Probe (FPP) because EIS produces more comprehensive data, can analyze electrochemical kinetic parameters related to the electrical elements of resistance (R), capacitance (C) and induction (L) of an electrode to AC potential signal at low amplitude (~10 mV) over a very wide frequency range, whereas FPP is limited to measuring its resistivity only. Identify the phase and its crystal structure by looking at the graph between the diffraction angle (2θ) and the intensity using an X'pert PRO PANalytical type XRD measuring instrument which has an X-ray diffract to meter of Cu Kα radiation with a wavelength of = 154060 Å in the range of 5° – 45°. The scan rate is with an angle of 0.01° from an X-ray source with a wavelength of 532 nm. The Identification of functional groups, ionic interactions with polymers based on the level of vibrational energy and rotation of the bonds using FTIR Thermo Scientific Nicolet iS10 type. The surface topography and sample size were generated by the SEM Type FEI Inspect S50 test, which is a three-dimensional photo of the sample surface.

2.3 Measurement of Electrical Conductivity of SPE Material Materials

Measurement of resistance and capacitance are properties of SPE using EIS type CS Series Electrochemical Workstation. The performing is at a frequency of 0.001 Hz to 100.000 Hz. Electrical conductivity is calculated using the equation:

$$\sigma = \frac{l}{Rs\ X\ A} \quad \text{.........} \quad (1)$$

With σ is SPE conductivity (S cm^{-1}), l is the thickness (cm), A is the area and Rs is the membrane resistance (Ω) as measured by EIS using the 2 probe DC method following Debye's response, as shown in Figure 3 below :

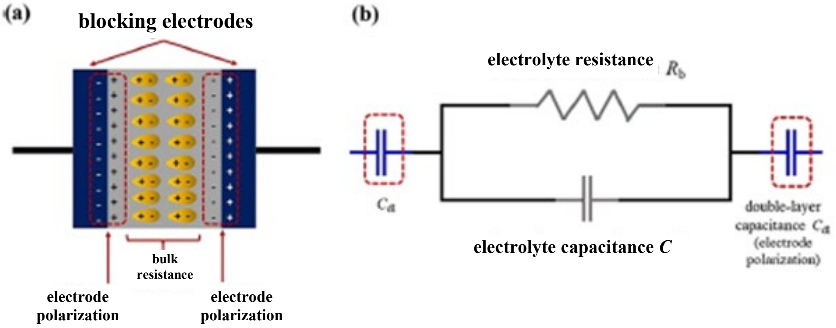

Fig. 3. (a) SPE depiction scheme with 2 blocking electrodes (b) Equivalent Circuit Model located between 2 blocking electrodes [25]

The measurement results is in the form of a Nyquist plot between the imaginary impedance (Z”) and the real impedance (Z') which shows the capacitance and resistance value of the material. The equivalent circuit obtained from this SPE is as shown in Figure 4 below:

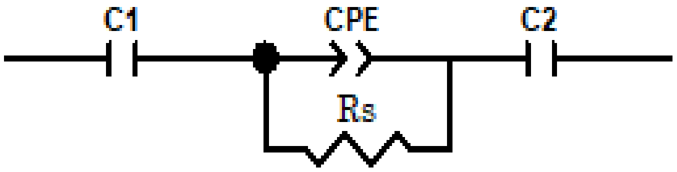

Fig. 4. Equivalent Circuit Material SPE Corn Starch.

The impedance value is obtained by fitting curve with the resulting imperfect semicircle graph so that CPE, C_1 and C_2 components are used to simulate the conductivity of the 2 probes used.

2.4 Results and Discussion

SPE data from research as shown in figure 5 below (a) CS (b) CS-Al (c) CS-Na

(a) (b) (c)

Fig. 5. SPE material synthesis results

The results of the diffraction pattern test of the cornstarch sample without aluminum nitrate salt showed 4 peaks in the diffraction pattern and with the addition of aluminum nitrate salt there were 3 peaks. This shows the lower crystallinity of the material (more amorphous). The amorphous peak is described as a broad and continuous peak [26].

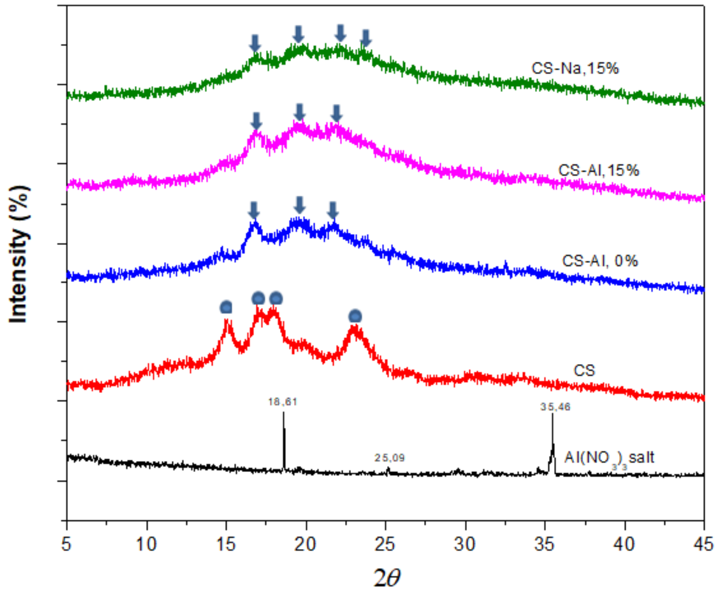

Fig. 6. Corn Starch SPE Diffractogram.

Figure 6 shows the initial condition of pure corn starch contained 4 peaks which were quite large after SPE formed with the addition of glycerol, the structure became they were more amorphous as indicated by the more gentle slope of the XRD spectrum, with the addition of salt there was a decrease in peak and shift. In the CS-Al 0% found 4 peaks at 2θ = 16.70°, 19.38°, 21.71° and 23.91° indicating type A corn starch [27]. At a concentration of 15%, only 3 peaks were found at 2θ = 16.78°, 19.28° and 21.94°, without the formation of new peaks and only experienced a shift, indicating a change to type B starch crystals [28]. The heated starch polymer causes a lot of water to be adsorbed, the hydrogen bonds between starch polymers weaken so that water is absorbed, making the size of the starch molecules increase. Heating to a temperature of 80oC gelatinization reaches its optimum some of the amylose begins to loosen so that the molecular chain structure becomes more open, amylose crystals expand up to 10 µm from containing 4 water molecules to 36 molecules per unit crystal cell, monolithic crystal type becomes hexagonal, the double helix chain becomes stranded parallel, so that a new crystal type polymorphy is formed from type A to type B [29]. The number of peaks in salt $(Al(NO_3)_3)$ was less than the baseline CS-Na 15% which still found 4 peaks at 2θ =16.83°, 19.56°, 22.19° and 23.79°. The less number of peaks formed indicates that SPE with the addition of aluminum nitrate is more amorphous than sodium acetate. The shift and the gentler slope of this peak is due to the insertion of ions from Al^{3+} into the corn starch crystals.

Based on the identification of functional groups, the results of the FTIR showed the presence of C-H bonded alkane group in the wavelength range of 2853 cm^{-1} – 2962 cm^{-1}, describing the content of corn starch as amylose hydrocarbon compound

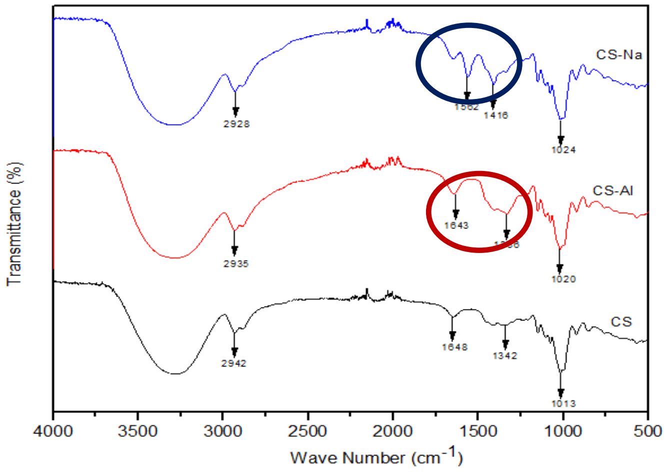

Fig. 7. Spectrum of FTIR SPE Corn Starch.

Figure 7 shows a clear difference in the appearance of the absorption peak, at the wavelength of 1336 cm^{-1} at CS-Al more widens than CS-Na, indicates the amilopectin more higher than amylose. Amylose is compactly arranged in the crystalline region while amylopectin is arranged in the amorphous region. Amorphous structure is formed because the fixation of nitrate compounds by corn starch. The nitrate ions are produced by aluminum nitrate compounds which dissociate into Al^{3+} ions and NO_3^- ions. It can be indicated CS-Al more amorphous than CS-Na.

Based on the SEM test image at Figure 8, it appears that at pure CS there are still white lumps which are the remnants of corn starch which are not all dissolved and undergo gelatinization, but after adding 15% aluminum nitrate salt (CS-Al), gelatinization and SPE homogenization are faster. This process have result a brighter structure indicating SPE already intercalated with aluminum nitrate salt ions. But there are also some in small amounts that have not been dissolved. In addition, cracks were found in the sample, this increases the contact surface area so that it can accommodate more ions . While in the CS-Na, in finding that there were wrinkles on the surface which indicated the smaller the contact surface so that it accommodated fewer ions than aluminum nitrate

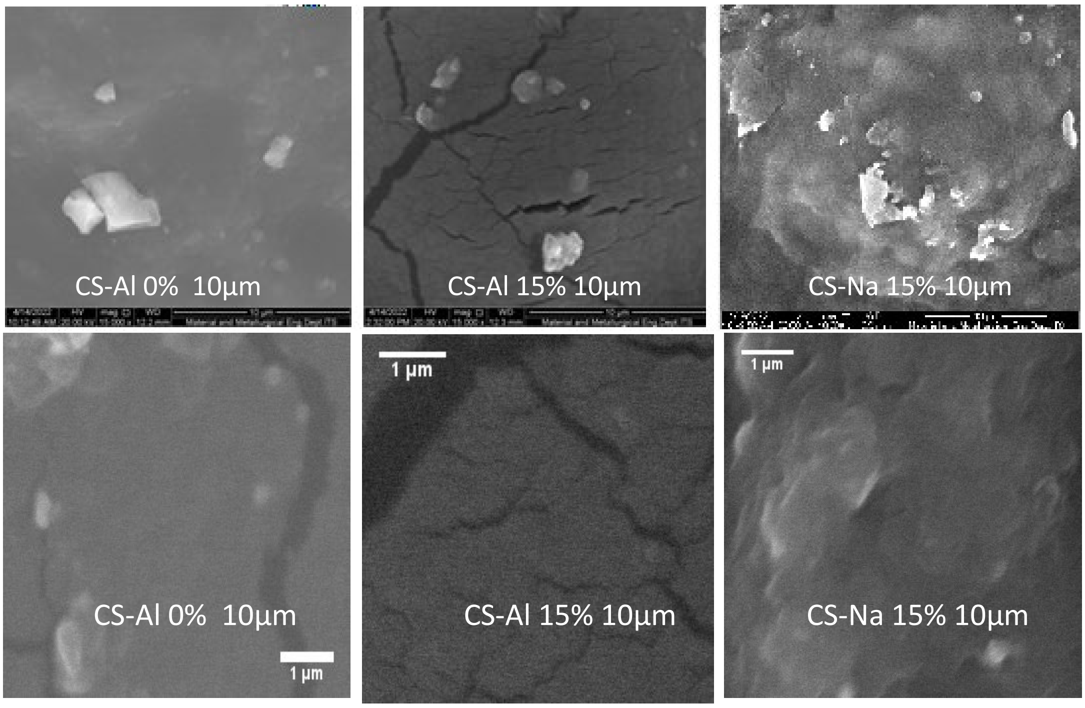

Fig. 8. SEM test results of SPE Corn Starch with a magnification of 15,000 X and measuring scale

Nyquist plot as a resulted EIS test of sample has show in almost the same impedance curve response forming a semicircular pattern.

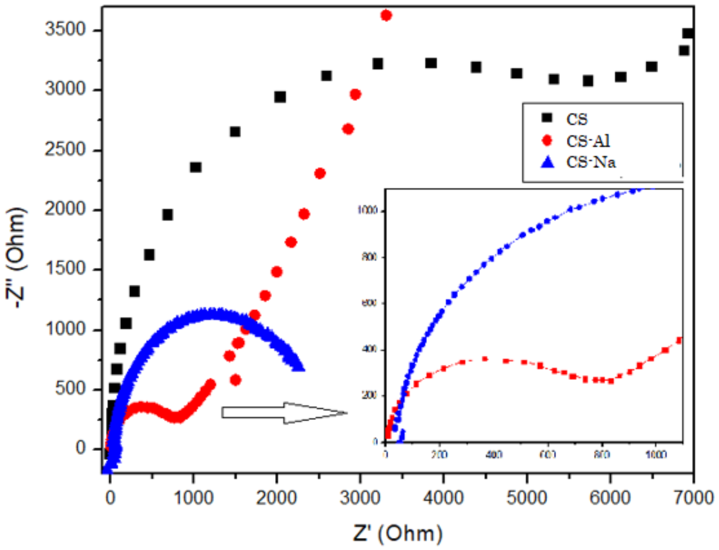

Fig. 9. Plot Results of Corn Starch SPE Nyquist

Figure 9 shows at a pure CS, it has a large semi-circle size which indicates a large impedance, after the addition of 15% aluminum nitrate salt, the semicircle tends to decrease drastically which means the conductivity is high. Compared to addition sodium acetate salt at the same concentration, is still smaller than aluminum nitrate. It meaning the conductivity SPE CS-Al more higher than CS-Na.

Based on the curve fitting of the Nquist plot graph pattern above, it was found the value Rs to determines the conductivity of this SPE, with values such as the following table:

Table 1. Results measurements SPE materials from equivalent circuit method

No	Concentration	l (cm)	A (cm^2)	Rs (Ω)	σ (S/cm)
1	CS-Al 0%	0,32 $x10^{-1}$	1	3620	8,84 $x10^{-6}$
2	CS-Al 15%	0,36 $x10^{-1}$	1	730	4,93 x 10^{-5}
3	CS-Na 15%	0,22 $x10^{-1}$	1	753,6	2,92 x 10^{-5}

Use equation 1, it appears that the conductivity of CS-Al is much greater than that of CS-Na with a value is almost twice of σ = 4,93 x 10^{-5} S/cm.

3. Summary

The synthesys of SPE had made from corn starch can be done by solution casting technique by heating in an oven for 9 hours at a temperature of 50ºC. This structure becomes stronger supported by the addition of glycerol. It was found that the conductivity value of CS-Al σ = 4,93 x 10^{-5} S/cm was greater than that of CS-Na whose value was σ = 2,92 x 10^{-5} S/cm. This is due to the SPE CS-Al show more amorphous structure which allow more flexible ionic segmental motion. This is also supported by XRD results which show that the addition of aluminum nitrate salt is more amorphous than sodium acetate, the shift in peak pattern is also greater due to the intercalation of Al^{3+} cations into corn starch. The results of FTIR found that there was fixation of nitrate compounds by corn starch, indicated a change in the hydroxyl group of corn starch amylopectin. The results of the SEM photos also shows that the surface structure is brighter and there are cracks that make the touch surface area larger so that the energy storage has a larger capacity. This makes it a good reference for developing SPE on Aluminum-ion batteries with aluminum nitrate salts.

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