Effect of Solid Polymer Electrolyte Based on Corn Starch and Lanthanum Nitrate on The Electrochemical Performance of Supercapacitor

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Abstract. Energy storage devices are crucial for reducing the consequences of intermittency. The supercapacitor is a promising energy storage device with outstanding properties such as high power density and long cycle life. A supercapacitor needs an electrolyte. We use solid polymer electrolyte (SPE) due to its safety, such as no leakage and no flammability. However, SPE has low ionic conductivity. The ionic conductivity of SPE can be improved by incorporating corn starch together with lanthanum nitrate (La(NO3)3) as additional materials in solid polymer electrolytes using the solution casting method. The SPE is then fabricated into a supercapacitor. The results of XRD characterization show that the 8wt.% concentration is increasingly amorphous characterized by a low degree of crystallinity value of 22.20%The electrochemical performance of the supercapacitor has been thoroughly investigated. The experimental results showed that the addition of 8 wt.% exhibits a suitable SPE for a supercapacitor. By electrochemical impedance spectroscopy (EIS) at room temperature, the maximum ionic conductivity of supercapacitor is 9.68×10^{-11} S/cm. The maximum specific capacitance from cyclic voltammetry is 2.71×10^{-7} F/g at a scan rate of 50 mV/s. The highest energy density and power density from galvanostatic charge-discharge are 0.032 Wh/kg and 3,402.13 W/kg. This research provides valuable insights for the further development of energy storage technology.

1 Background

The reduction of carbon emissions in various sectors is an issue that has been the subject of ongoing debate. The promotion of the use of renewable energy can be one way of being part of the solution to the problem of carbon emissions. Some examples of renewable energy are solar energy, geothermal energy, wind energy, and ocean energy (sea waves) [1]. However, because it depends on natural conditions, this energy is only available intermittently. For example, solar energy is available during the day but not at night. Hence, there is a need for advanced energy storage technology.

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Fuel cells, batteries, capacitors, and supercapacitors are examples of electrochemical energy storage systems [2]. Low power density, lengthy recharge times, short cycle lives, and environmental issues are just a few of the disadvantages of battery systems. By using supercapacitors, these restrictions can be overcome [3]. They can reduce pollution brought on by greenhouse gases and have a high power density of 10 kW kg-1 [4].

Electrolytes are necessary for the transfer of charge between the anode and cathode in supercapacitors [5]. Ionic liquids (ILs) and aqueous electrolytes are examples of liquid electrolytes that are commonly used [5, 6, 7]. But there's a chance of leaks, fires, or explosions with these liquid electrolytes [8]. There are other kinds of electrolytes, like solid electrolytes. One type of solid electrolyte that offers several advantages is called a solid polymer electrolyte (SPE), which also has good safety ratings, outstanding flexibility, and exceptional thermal stability [8].

These solid electrolyte-forming materials can be produced through natural polymers. One of the natural polymer materials is starch. Types of starch are arrowroot (amylose 15%), rice (amylose 17%), tapioca (amylose 18%), potato (amylose 22%), wheat (amylose 24%), and corn (amylose 27%). Since corn starch contains high levels of amylose, it can be used as an option for solid electrolyte-forming material. Starch that has a high amylose content is considered more suitable for making starch and salt electrolytes. The straight structure of amylose allows the salt to bind more strongly to the starch, resulting in better conductivity and charge storage ability [9] Corn starch has advantages such as being biodegradable, low-cost, abundant in nature, non-toxic, and having a high solubility in water [10].

Additional components are required in electrolytes to improve ionic conductivity. Ionic conductivity can be increased by adding conducting ions to the electrolyte using lanthanum nitrate ($La(NO_3)_3$). Hamidah et al. added a trace amount of $La(NO_3)_3$ to the graphene oxide (GO) membrane material in their study. Increased conductivity results from an ionic interaction between oxygen functional groups on GO nanosheets and lanthanum cations caused by this addition [11]. In a study by Zhao et al. (2022), 0.0085 M of lanthanum nitrate was added to a 2 M solution of zinc sulfate electrolyte ($ZnSO_4$). Their investigation's findings demonstrate that this addition led to electrodeposition on the zinc, which enhanced the battery's performance and cycle life. $La(NO_3)_3$ has also been discovered to have further applications as an electrolyte additive, such as stabilizing the surface morphology of lithium anodes in lithium-sulfur batteries, which makes the battery more effective [12].

SPE synthesis can be done using phase inversion, photopolymerization, electrospinning, and solution casting methods. The solution casting or solvent casting method is the simplest and easiest way to make electrolyte films [13].

The research gap in this study lies is the inadequate research into solid polymer electrolytes (SPEs) for supercapacitors which incorporate lanthanum nitrate and corn starch as primary components. Although the benefits of SPEs are well known, there is a lack of research that focuses on the synthesis and electrochemical effects of SPEs made from corn starch and improved with lanthanum nitrate for use in supercapacitors.

Many techniques are used as we go into the synthesis of solid polymer electrolytes, but the solution casting approach that was selected stands out for its effectiveness and simplicity. This technique becomes an important part of our work as we try to close the current research gap on the use of corn starch and lanthanum nitrate in solid polymer electrolytes designed for supercapacitors.

This work aims to synthesize a solid polymer electrolyte, analyze its crystallographic properties, investigate its influence on the electrochemical performance of supercapacitors.

This research is worthwhile as it will help create sustainable energy storage options in addition to tackling environmental issues associated with carbon emissions. The innovative application of solid polymer electrolytes to enhance supercapacitor performance may boost its performance, which highlights the significance and urgency of our studies.

2 Methodology

2.1 Synthesis of Solid Polymer Electrolyte (SPE)

The SPE synthesis process employs the solution casting technique. Initially, lanthanum nitrate ($La(NO_3)_3$) was dissolved in a beaker containing 25 ml of H_2O at varying concentrations of 0%, 4%, 8%, 16%, 20%, and 25%. The solution was then stirred for 5 minutes at 200–250 rpm. To prevent clotting, 0.57 ml of glycerol and 1.5 grams of corn starch were added, followed by further stirring. The beaker was sealed and covered with plastic wrap, then placed inside a water bath and magnetic stirrer hot plate, with temperatures reaching up to 80–90 °C and 200–250 rpm, until the solution became homogeneous for one hour. After removing the solution from the beaker, any remaining bubbles were eliminated through cooling. The solution was then poured into a petri dish, followed by evaporation in an oven for 6–9 hours at 50 °C. The solution was then poured into a petri dish, followed by evaporation in an oven for 6–9 hours at 50 °C. This allows for solid formation, producing SPE films.

Table 1 presents material data for SPE synthesis requirements including data on the composition of corn starch and lanthanum nitrate. The composition of lanthanum nitrate can be calculated from the given equation:

$$wt.\% = \frac{a}{a+b} x100 \quad (1)$$

Where:
(1)
a : the amount of $La(No_3)_3$ (gram)
b : the amount of corn starch (gram)

Table 1. Composition of SPE from Starch and Lanthanum Nitrate

$La(No_3)_3$ (wt.%)	$La(No_3)_3$ (g)	Corn Starch (g)	Solvent	
			Glycerol (ml)	H_2O (ml)
0	0	1.5	0.57	25
4	0.063	1.5	0.57	25
8	0.131	1.5	0.57	25

Figure 1 illustrates the SPE synthesis process carried out at The Energy Engineering and Environmental Conditioning Laboratory, Engineering Physics, ITS.

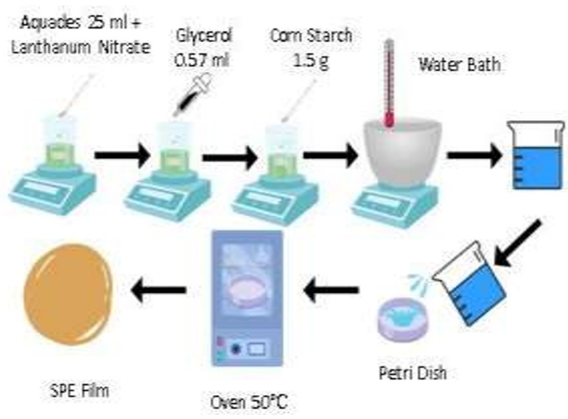

Fig. 1. SPE Synthesize Process

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2.2 Characterization of SPE Materials

The SPE samples were characterized for amorphousness and crystallinity using XRD by PanAnalytical-type E'xpert PRO using a wavelength of 1.54056 Å and Ni filter, 40 kV, and 100 mA of CuKα radiation. All samples were analyzed in the range 2θ =5°–80°, with a scanning speed of 0.5 °C/min and 0.05°/step at room temperature. SPE samples were characterized using Thermo Scientific Nicolet iS10 type FTIR to identify functional groups, ionic interactions of corn starch, and La(NO3)3. The SPE samples were characterized using the DSC of the Mettler Toledo brand with a scan rate of 10 °C/min and a temperature of 25 °C–150 °C.

2.3 Electrode Preparation and Supercapacitor Fabrication

The electrode used is an activated carbon electrode made from graphite, namely Cu Foil Single Coated By CMS Graphite 241L x 200W x 0.1T mm. Graphite electrode as anode and cathode at the same time.

Fabrication on supercapacitors is done by making coin cells, as shown in Figure 2. The fabricated supercapacitor is a symmetric supercapacitor or has the same material for the anode and cathode. Fabrication on supercapacitors is carried out in an open room. The first thing to do is put the cell-cap (small) then the anode electrode. Then it was stacked with SPE. Because the electrolyte used is SPE-type, the supercapacitor does not require a separator. The next step is to place the cathode, spacer, and spring. Then closed with a cell-cap (large). The coin cell is then pressed using a crimping machine with a minimum pressure of 0.5 Mpa to 1 Mpa.

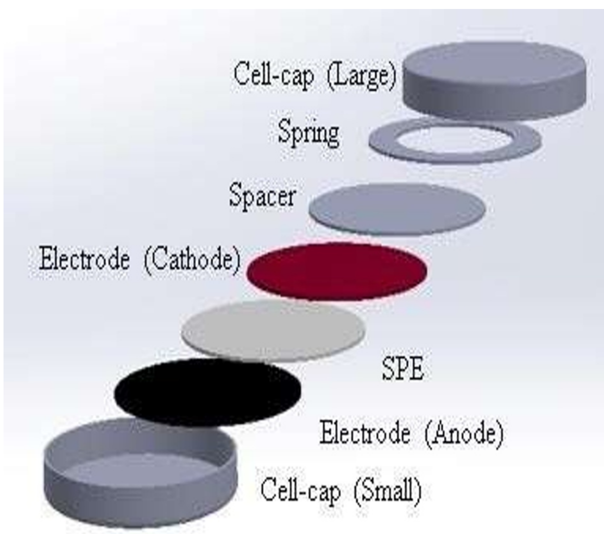

Fig. 2. Supercapacitor Fabrication

2.4 Electrochemical Performance Test on SPEs and Supercapacitors

EIS tests on supercapacitors were carried out at room temperature and elevated temperature. EIS test was conducted at a frequency of 0.01 Hz to 1000000 Hz. EIS testing was carried out to determine the value of ionic conductivity in the sample. The following is the equation of ionic conductivity.

$$\sigma = \frac{l}{R_b x A} \quad (2)$$

Where:
σ : Ionic conductivity (S/cm)
l : Thickness of SPE film (cm)
R_b : Bulk Resistance (Ω)
A : Area (cm^2)

The value of Rb is obtained from the Nyquist Plot curve fitting. Curve fitting is done through Zview software by creating an equivalent circuit.

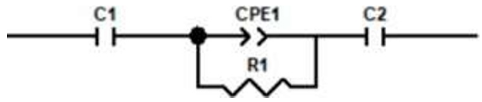

Fig. 3. Equivalent Circuit

3 Result and Discussion

The XRD test was carried out to determine the degree of crystallinity and amorphous phase in the sample. The data obtained is in the form of a diffraction pattern graph, which will then be analyzed. The diffraction pattern graph is shown in figure 4. The diffraction pattern graph of corn starch without any additional material has four diffraction peaks at 15.10˚, 17.19˚, 18.0˚, and 23.0˚. Corn starch is type A [14]. However, the addition of glycerol turns corn starch into type B [15]. The addition of glycerol aims to act as a plasticizer because starch does not have the ability to act as a plastic. In addition, starch also has limitations, such as poor mechanical properties [15, 16]. The degree of crystallinity can be found with this following equation.

$$X_C = \frac{A_C}{A_T} x\ 100\% \quad (3)$$

Where:
X_C : Degree of crystallinity
A_C : Area of the crystalline peak
A_T : Total area of the amorphous peak and the crystalline peak

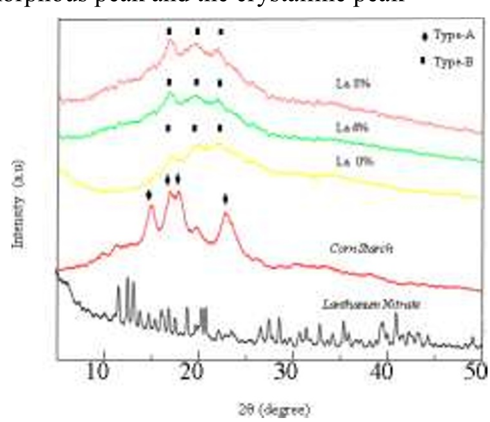

Fig. 4. XRD Graph for Lanthanum Nitrate, Corn Starch, La 0% to La 8%

The variation in $La(NO_3)_3$ concentration, namely 0wt.%, 4wt.%, and 8wt.%, represent crystallinity degrees of 27.28%, 23.24%, and 22.20%, in that order. The degree of crystallinity has been seen to decrease, which implies the increase of amorphous phases [15]. The existence of an amorphous phase is essential for polymer electrolytes since it reduces crystallinity and increases ionic conductivity [17].

According to these results, an electrolyte concentration of 8% seems to work best for better supercapacitor performance. This concentration causes a significant reduction in the degree of crystallinity, which improves the material's amorphous characteristics and, as a result, its overall performance.

The EIS test uses frequencies from 0.01 Hz to 1,000,000 Hz.The EIS test was carried out to determine the ionic conductivity. To get the ionic conductivity value, we need the R_b (bulk resistance) value. The Rb value is obtained by fitting the curve using the equivalent cirquit. At La 0%, the ionic conductivity value is 2.89×10^{-11} S/cm. La 4% is 3.50×10^{-11} S/cm and La 8% is 9.68×10^{-11} S/cm. It can be seen if the higher the salt concentration, the higher the ionic conductivity. Increased ion density, a wider range of electrolyte potentials, and stability of the supercapacitor at high voltages are thought to be the mechanisms behind the improvement of ionic conductivity in supercapacitors [18, 19]. The amount of charge carriers, ion mobility, and ion valency all affect the electrolyte's ionic conductivity [18].

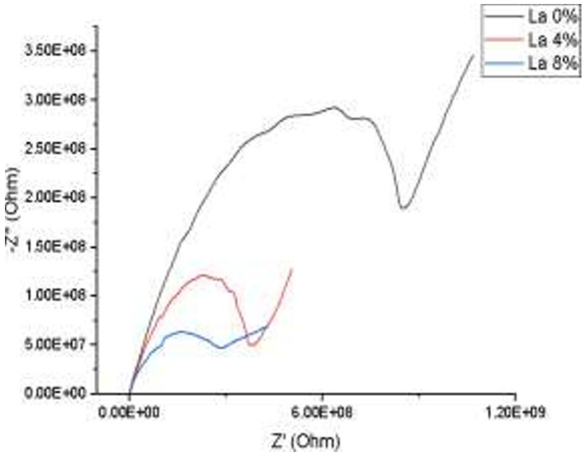

Fig. 5. Nyquist Plot for La 0%, La 4%, La 8%

The CV test was performed for 5 cycles with a scan rate of 50 mV/s. From the CV curve, the specific capacitance values were 1.48×10^{-9} F/g for La 0%, 1.01×10^{-8} F/g for La 4%, and 2.71×10^{-7} F/g for La 8%. It can be seen from the CV curve (figure 6) that the greater the area, the higher the specific capacitance. The ion diffusion rate affects the electrode's specific capacitance; a greater diffusion rate results in a higher specific capacitance [20].

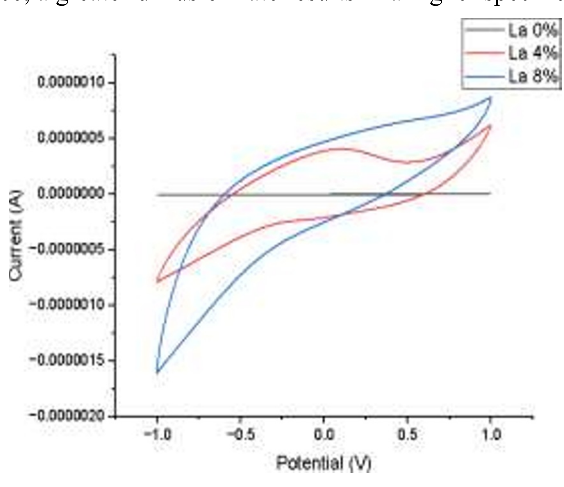

Fig. 6. The CV curves of supercapacitor at scan rate 50 mV/s

GCD was performed to determine the performance of the supercapacitor. GCD was performed on 5 cycles with a c-rate of 0.5 and at various current. The current used was 0.0039899 A (La 0%), 0.0038845 A (La 4%), and 0.0039021 A (La 8%). From the GCD test, a GCD curve is obtained, which shows how the supercapacitor charges and discharges energy. At La 0% has an energy density of 0.024 Wh/kg and a power density of 2,501.61 W/kg. At La 4 % has an energy density of 0.028 Wh/kg and a power density of 2,885.62 W/kg. From the GCD curve, it is known that the La 8% sample is the sample with the highest energy density and power density values, namely 0.032 Wh/kg and 3,402.13 W/kg. The high energy density value indicates the ability of supercapacitors in the La 8% sample to store energy in a larger amount. The high power density value indicates that the supercapacitor has a fast charging and discharging time.

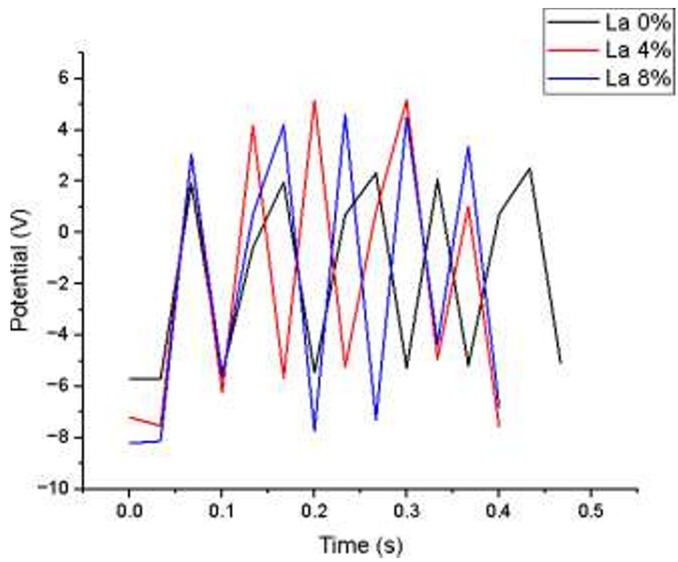

Fig. 7. The GCD curves of supercapacitor

4 Conclusion

In summary, the purpose of this study was to optimize the performance of supercapacitors by carefully adjusting the electrolyte compositions of lanthanum nitrate that is incorporated with corn starch. The degree of crystallinity decreased as the concentration of $La(NO_3)_3$ increased, indicating the inclusion of amorphous phases, which are essential for increased ionic conductivity in polymer electrolytes.

The EIS results showed an increase in ionic conductivity with higher $La(NO_3)_3$ concentrations, which could be attributed to mechanisms such as increased ion density and a wider electrolyte potential range. The CV and GCD tests further validated the superior performance of the La 8% sample, showing enhanced specific capacitance, energy density, and power density. The GCD curves confirmed the La 8% sample's ability to efficiently charge and discharge energy, making it a promising candidate for high-performance supercapacitors.

To summarise, the supercapacitor's overall performance was significantly improved upon by the optimised electrolyte composition of 8% $La(NO_3)_3$. This highlights the significance of customised electrolyte formulations in obtaining higher energy storage capacities. The results provide important new information for the creation of sophisticated energy storage devices that may be used in many different technical fields.

References

1. Neha, & Joon, R. (2021). Renewable Energy Sources: A Review. *Journal of Physics: Conference Series*, *1979*(1), 012023. https://doi.org/10.1088/1742-6596/1979/1/012023
2. Ragupathy, P., Bhat, S. D., & Kalaiselvi, N. (2023). Electrochemical energy storage and conversion: An overview. *WIREs Energy and Environment*, *12*(2), e464. https://doi.org/10.1002/wene.464
3. Olabi, A. G., Abbas, Q., Al Makky, A., & Abdelkareem, M. A. (2022). Supercapacitors as next generation energy storage devices: Properties and applications. *Energy*, *248*, 123617. https://doi.org/10.1016/j.energy.2022.123617
4. Benoy, S. M., Pandey, M., Bhattacharjya, D., & Saikia, B. K. (2022). Recent trends in supercapacitor-battery hybrid energy storage devices based on carbon materials. *Journal of Energy Storage*, *52*, 104938. https://doi.org/10.1016/j.est.2022.104938
5. Pal, B., Yang, S., Ramesh, S., Thangadurai, V., & Jose, R. (2019). Electrolyte selection for supercapacitive devices: A critical review. *Nanoscale Advances*, *1*(10), 3807–3835. https://doi.org/10.1039/C9NA00374F
6. Yu, L., & Chen, G. Z. (2019). Ionic Liquid-Based Electrolytes for Supercapacitor and Supercapattery. *Frontiers in Chemistry*, *7*, 272. https://doi.org/10.3389/fchem.2019.00272
7. Iqbal, M. Z., Zakar, S., & Haider, S. S. (2020). Role of aqueous electrolytes on the performance of electrochemical energy storage device. *Journal of Electroanalytical Chemistry*, *858*, 113793. https://doi.org/10.1016/j.jelechem.2019.113793
8. Yao, P., Yu, H., Ding, Z., Liu, Y., Lu, J., Lavorgna, M., Wu, J., & Liu, X. (2019). Review on Polymer-Based Composite Electrolytes for Lithium Batteries. *Frontiers in Chemistry*, *7*, 522. https://doi.org/10.3389/fchem.2019.00522
9. Chauhan, J. K., Yadav, D., Yadav, M., Kumar, M., Tiwari, T., & Srivastava, N. (2020). NaClO4 added, corn and arrowroot starch based economical, high conducting electrolyte membranes for flexible energy devices. *SN Applied Sciences*, *2*(5), 899. https://doi.org/10.1007/s42452-020-2660-0
10. Khiar, A. S. A., Anuar, M. R. S., & Md Parid, M. A. (2016). Effect of 1-Ethyl-3-Methylimidazolium Nitrate on the Electrical Properties of Starch/Chitosan Blend Polymer Electrolyte. *Materials Science Forum*, *846*, 510–516. https://doi.org/10.4028/www.scientific.net/MSF.846.510
11. Hamidah, N. L., Shintani, M., Ahmad Fauzi, A. S., Mission, E. G., Hatakeyama, K., Quitain, A. T., & Kida, T. (2019). Improving the proton conductivity of graphene oxide membranes by intercalating cations. *SN Applied Sciences*, *1*(6), 630. https://doi.org/10.1007/s42452-019-0641-y
12. Liu, S., Li, G.-R., & Gao, X.-P. (2016). Lanthanum Nitrate As Electrolyte Additive To Stabilize the Surface Morphology of Lithium Anode for Lithium–Sulfur Battery. *ACS Applied Materials & Interfaces*, *8*(12), 7783–7789. https://doi.org/10.1021/acsami.5b12231
13. Teo, L. P., Buraidah, M. H., & Arof, A. K. (2021). Development on Solid Polymer Electrolytes for Electrochemical Devices. Molecules, 26(21), 6499. https://doi.org/10.3390/molecules26216499
14. Dome, K., Podgorbunskikh, E., Bychkov, A., & Lomovsky, O. (2020). Changes in the Crystallinity Degree of Starch Having Different Types of Crystal Structure after Mechanical Pretreatment. *Polymers*, *12*(3), 641. https://doi.org/10.3390/polym12030641
15. Wang, B., Xu, X., Fang, Y., Yan, S., Cui, B., & Abd El-Aty, A. M. (2022). Effect of Different Ratios of Glycerol and Erythritol on Properties of Corn Starch-Based Films. *Frontiers in Nutrition*, *9*, 882682. https://doi.org/10.3389/fnut.2022.882682

16. Surendren, A., Mohanty, A. K., Liu, Q., & Misra, M. (2022). A review of biodegradable thermoplastic starches, their blends and composites: Recent developments and opportunities for single-use plastic packaging alternatives. *Green Chemistry*, *24*(22), 8606–8636. https://doi.org/10.1039/D2GC02169B
17. St-Onge, V., Cui, M., Rochon, S., Daigle, J.-C., & Claverie, J. P. (2021). Reducing crystallinity in solid polymer electrolytes for lithium-metal batteries via statistical copolymerization. *Communications Materials*, *2*(1), 83. https://doi.org/10.1038/s43246-021-00187-2
18. Mendhe, A., & Panda, H. S. (2023). A review on electrolytes for supercapacitor device. *Discover Materials*, *3*(1), 29. https://doi.org/10.1007/s43939-023-00065-3
19. Kwon, H.-N., Jang, S.-J., Kang, Y. C., & Roh, K. C. (2019). The effect of ILs as co-salts in electrolytes for high voltage supercapacitors. *Scientific Reports*, *9*(1), 1180. https://doi.org/10.1038/s41598-018-37322-y
20. Mai, L., Li, H., Zhao, Y., Xu, L., Xu, X., Luo, Y., Zhang, Z., Ke, W., Niu, C., & Zhang, Q. (2013). Fast Ionic Diffusion-Enabled Nanoflake Electrode by Spontaneous Electrochemical Pre-Intercalation for High-Performance Supercapacitor. *Scientific Reports*, *3*(1), 1718. https://doi.org/10.1038/srep01718