Hydrothermal LiTiO$_2$ Cathode and Polyurethane Binder of High Current Lithium Ion Batteries

Vega Fresamitia Ingried [a], Sri Haryati [b], Nirwan Syarif [c,*]

[a] Magister Degree Program, Chemical Engineering Department, Faculty of Engineering, Sriwijaya University, Indonesia
[b] Chemical Engineering Department, Faculty of Engineering, Sriwijaya University, Indonesia
[c] Center of Research Excellent in Fuel Cell and Hydrogen, Universitas Sriwijaya, Indonesia
Corresponding author: *nsyarif@unsri.ac.id

Abstract - **This research is to prepare a lithium-ion battery using carbon-based water spinach rods as anode and LiTiO$_2$ as a cathode. Carbon and LiTiO$_2$ are used as electrodes to produce lithium-ion batteries on a laboratory scale. Carbon derived from water spinach produces more economic value and is easy to obtain. The electrolytes used are liquid and gel-based LiCl with 10%, 20%, and 40% concentrations. The binder used to prepare lithium-ion batteries is a polyurethane (PU) binder. Lithium-ion batteries (LIBs) are arranged as anode-separator/electrolyte-cathode. The battery was tested with a potentiostat in cyclic voltammetry and galvanostatic modes. In cyclic voltammetry measurements, the value of the current in the lithium-ion battery and the plot on the cyclic voltammetric graph can be used to calculate the value of power and energy. Galvanostatic measurement aims to determine the time it takes to charge and discharge the lithium-ion battery. The measurement of cyclic voltammetry on the performance of lithium-ion batteries shows the highest current value found in batteries with a liquid electrolyte media concentration of 40% by 0.18A, while the lowest current value is found in batteries with a 10% concentration gel electrolyte media of 0.004A. The highest power and energy values are found in batteries with a liquid electrolyte media concentration of 20%. The lowest power and energy values are found in batteries with 10% concentration gel electrolyte media. In the galvanostatic measurement, a graph of charging and discharging lithium-ion batteries is produced. The fastest charging slope is in the battery, with a liquid electrolyte media concentration of 40%. The slope discharge of liquid electrolyte media with a concentration of 40% is the fastest compared to other types of batteries. Batteries with 10% concentration gel electrolyte media become the batteries with the longest charging slope and the longest discharge slope compared to other types of batteries.**

Keywords - **Lithium-Ion Batteries (LIBs); carbon; LiTiO$_2$; cyclic voltammetry; galvanostatic.**

I. INTRODUCTION

Batteries can be used as energy storage and where electrochemical reactions occur [1]. Therefore, the essential ingredients of making battery electrodes affect batteries' ability to store energy and electrochemical reaction processes [2]. The primary material that can be used to make battery electrodes is carbon [3]. In general, carbon can be easily produced and has economic value [4], so that this research will utilize carbon-based water spinach rods as anodes and LiTiO$_2$ as cathodes to produce electrodes for laboratory-scale lithium-ion batteries. A good carbon electrode must have pores and have few functional group bonds. This aims to facilitate the process of capturing and releasing ions so that electric current can flow [5].

The lithium-ion battery (LIB) is a technology that is being developed at present and is widely used in various electronic devices. This is because lithium-ion batteries have a high energy value and a flexible design [6]. Reversible reactions are a significant advantage of lithium-ion batteries. This reversible reaction to the lithium-ion battery causes the lithium-ion battery to be recharged when the battery is discharged. When the battery is discharged, the ion will move from the anode to the cathode. Conversely, when a battery is charging, the ion will move from the cathode to the anode [7]. A battery's ability to produce an electric current can be tested with a potentiostat to measure cyclic voltammetry and galvanostatic charging-discharging [8]. Therefore, the development and testing of batteries using carbon from the water spinach rods should be investigated.

In this study, to make a high current value in lithium-ion batteries, an electrode material that has a high conductivity value is needed [9]. High conductivity values can be generated from polyurethane (PU) binders and metallic material elements such as $LiTiO_2$, which will be used as cathodes in lithium-ion batteries (LIBs) [10]. This study prepared $LiTiO_2$ electrodes as cathodes produced from hydrothermal processes and prepared carbon-based-water spinach rod electrodes as anodes with hydrothermal and pyrolysis processes polyurethane (PU) binders.

The lithium-ion battery varied the concentration of the LiCl electrolyte and the electrolyte media. The concentrations of the LiCl electrolyte used were 10%, 20%, and 40%. Meanwhile, the electrolyte media used were liquid media and gel media. This research produced 6 types of batteries that to be tested for their work performance with cyclic voltammetry and galvanostatic measurements.

Cyclic voltammetry measurement aims to determine the value of the current produced by the battery [11]. The current value is generated due to some ions moving from one point to another in a series [12]. A well-performing lithium-ion battery will produce a high current rating [13]. Galvanostat measurement aims to determine the time required for lithium-ion batteries in the charging and discharging process [14]. A good battery has less time to charge and has a longer time to discharge [15].

II. Materials and Methods

A. Materials

The materials used in this study were carbon-based water spinach rods, $LiTiO_2$, LiCl, polyvinyl alcohol (PVA), polyethylene terephthalate (PET), and Potentiostat Dummycell.

B. Methods

1) Carbon Preparation: The material used to produce carbon is water spinach rods that have been cleaned and dried using an oven. Water spinach rods that have dried and then ground using a disk mill from JIMO-FF 15 and filtered with a size of 100 mesh, resulting in water spinach rods powder. Water spinach rods powder, then hydrothermal and pyrolysis to produce carbon that has pores.

2) LiTiO₂ Preparation: Cathode preparation for the battery is done by dissolving 8.4 grams of lithium chloride (LiCl) into 40 ml of deionized water. The solution is then mixed with 0.4 grams of TiO_2 and 0.1 grams of NaOH. Then, the mixture is placed into a hydrothermal reactor and heated at 180ºC in a furnace for 24 hours.

3) Battery Preparation: Battery preparation is carried out by preparing copper sheets, carbon-based water spinach rods as anodes, and $LiTiO_2$ as cathodes. The anode and cathode are mixed with a polyurethane (PU) binder, so they are in the form of a paste. Each paste with a size of 2.5 × 2.5 cm is then coated on a sheet of copper measuring 3 × 3 cm using a doctor blade and dried to produce electrodes for lithium-ion batteries.

Battery preparation with liquid media LiCl electrolytes is carried out by arranging the anode-separator/electrolyte-cathode and placed in a polyethylene terephthalate (PET)

pocket. LiCl electrolytes with liquid media were prepared at concentrations of 10%, 20%, and 40%. Preparation of anode, separator/electrolyte, cathode, and polyethylene terephthalate (PET) then vacuums and separates a small hole that functions to enter the liquid electrolyte. Inserting liquid electrolyte into the battery is carried out by injection using a glovebox.

Battery preparation with gel media LiCl electrolytes is carried out by preparing polyvinyl alcohol (PVA), each containing 10%, 20%, and 40% LiCl. The preparation for a gel media electrolyte battery is the same as that for a liquid media electrolyte battery. After being arranged in the same order as the liquid media electrolyte battery, The battery is then vacuumed without leaving a small hole because the gel media can be directly coated between the anode and cathode so that the gel functions as well as a separator.

4) Battery Performance Testing: Battery performance testing is performed using a dummy cell potentiostat, where a dummy cell potentiostat is used to measure cyclic voltammetry and galvanostatic [8]. In cyclic voltammetry, measurements are carried out in full-cell mode, where the battery anode is connected to the counter electrode probe, and the battery cathode is connected to the electrode probe that works from the potentiostat [16]. Currently used to measure voltage in cyclic voltammetry measurements ranges from -3 to 3 volts. Cyclic voltammetry measurements are carried out to determine the oxidation-reduction reaction in the battery by producing a graph between the current (I) against the voltage (V). The value formed in the current (I) and voltage (V) can be used to find the value of power (P) and energy (E) produced by the battery [17]. The formula that can be used to find the values of power (1) and energy (2) is as follows:

$$P = I \times V \tag{1}$$
$$E = \int I \times V \, dt \tag{2}$$

Galvanostat measurements are performed to determine the charging and discharge slope's value on the battery [14]. In the galvanostatic charging-discharging measurement, the galvanostat mode and the connected connection are the same as the cyclic voltammetric measurement [18]. But the current value during the galvanostat measurement process is changed from -2 mA to 7 mA.

III. Results and Discussions

Batteries consist of anodes, cathodes, and electrolytes, which function to deliver ions [19]. In this study, the anode used was carbon-based water spinach rods and the cathode used was $LiTiO_2$. The type of electrolyte used is LiCl with a concentration variation of 10%, 20%, and 40% with liquid and gel media, respectively. The type of binder used is a polyurethane (PU). Thus, the total battery to be tested for cyclic voltammetry and galvanostatic charging-discharging are six batteries.

A. Cyclic Voltammetry

Cyclic voltammetry measurements are carried out one by one on each battery. In cyclic voltammetry, measurements produce graph lines that flow from low to high and from high to low. Current flow from low to high shows anodic flow, and peaks that form in anodic flow show reduction reaction. Conversely, high to low flow indicates cathodic flow and

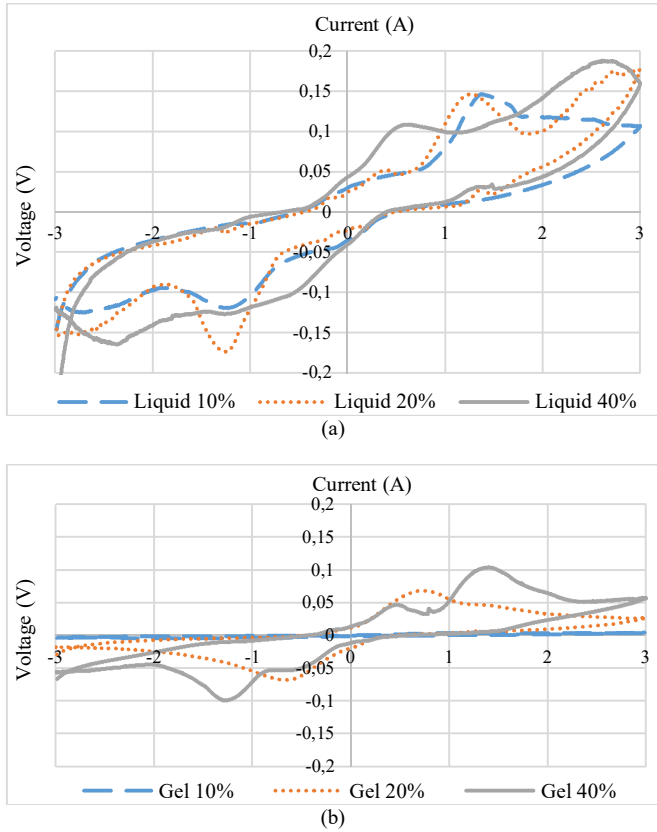peaks formed in cathodic flow indicate oxidation reactions [20].

Fig. 1 Cyclic Voltammetry Graph of Lithium-Ion Batteries (a) Liquid Electrolyte Media and (b) Gel Electrolyte Media

In Figure 1, the cyclic voltammetry graph shows the difference in the value of the current produced in each lithium-ion battery. Lithium-ion batteries with liquid electrolytes produce the highest current values at a concentration of 40% with a value of 0.18A. In liquid electrolyte lithium-ion batteries with a concentration of 10% and 20% the value of the current produced each concentration is 0.14A and 0.17A. In lithium-ion batteries with gel electrolytes, the highest current value at a concentration of 40% with a value of 0.10A. Whereas, in gel electrolyte lithium-ion batteries with a concentration of 10% and 20%, the value of the current produced for each concentration was 0.004A and 0.06A.

Several factors cause the difference in the current value of lithium-ion batteries; among the factors that influence the type of electrolyte media, liquid electrolyte media produce higher current values than the gel electrolyte media [8]. This is because the movement of Li^+ ions in gel electrolytes is more difficult to mobility, so the capture and release of Li^+ ions are challenging to work optimally. Meanwhile, in liquid electrolyte media, Li^+ ions are easier to mobilize in capturing and releasing Li^+ ions [21]. Therefore, the liquid electrolyte media's current value is higher than the current value in the gel electrolyte media [22]. This also applies to the value of concentration with increasing concentration, then the value of the resulting current also continues to increase. The increasing number of Li+ ions causes this process of capturing and releasing Li^+ ions in the anode and cathode pores can work optimally [23].

Variable		Parameter	
Electrolyte Media	Electrolyte Concentration (%)	Energy (W.h)	Power (W)
Gel	10	4.67×10^{-7}	1.38×10^{-5}
Gel	20	3.91×10^{-6}	1.16×10^{-4}
Gel	40	9.30×10^{-4}	2.75×10^{-2}
Liquid	10	1.30×10^{-3}	3.85×10^{-2}
Liquid	20	4.83×10^{-3}	1.43×10^{-1}
Liquid	40	4.77×10^{-5}	1.41×10^{-3}

In Table 1, the value of power and energy can be calculated using the formulas (1) and (2) of the CV profile (voltammogram), where a good lithium-ion battery will produce high power and energy values [17]. The highest power and energy values are in the liquid electrolyte media with a concentration of 20%, while the lowest power and energy values are found in the gel electrolyte media with a concentration of 10%. This is influenced by electrolyte media, LiCl concentration, and the pressing process on lithium-ion batteries. The pressing process that is done incorrectly can affect the power and energy values in the lithium-ion battery [8].

B. Galvanostatic Charging – Discharging

Batteries tested for cyclic voltammetry will be retested by galvanostatic charging-discharging with a measurement time span of 200 seconds. Galvanostatic charging-discharging measurement is carried out to determine the profile of charging and discharging the lithium-ion battery [24].
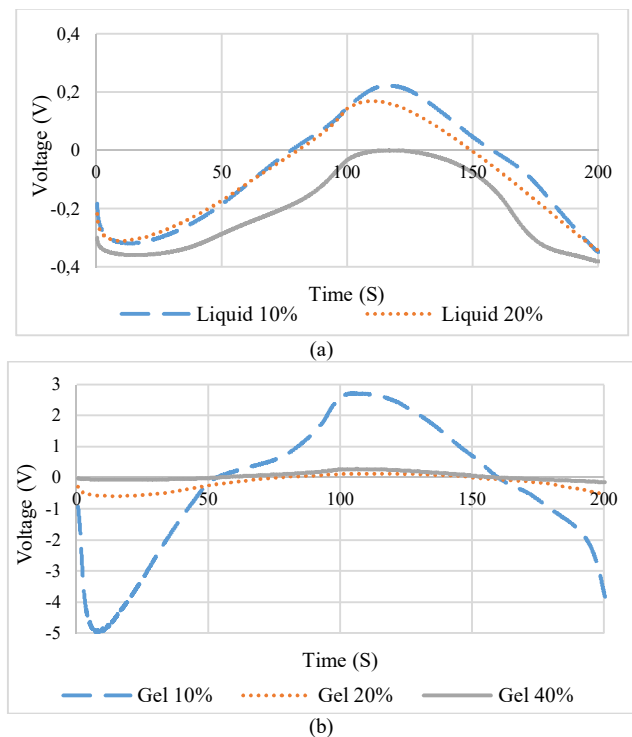

Fig. 2 Galvanostatic charging-discharging Graph of Lithium-Ion Battery (a) Liquid Electrolyte Media and (b) Gel Electrolyte Media

Figure 2 shows the process of charging and discharging a battery that has different levels according to the slope of the line. The rising galvanostat graph shows the battery charging, and the decreasing galvanostat graph shows the battery discharging [25]. The steeper line on the galvanostat graph shows that the charging and discharging process is getting faster. Conversely, if the lines on the galvanostat ramps are sloping, the battery charging and the discharging process tends to be slower [8]. In this study, the charging and discharging process time is proportional to the battery, meaning that if the battery charging time tends to be longer, then the battery discharging process also tends to be extended. Conversely, if the battery charging process tends to be fast, then the battery discharging process also tends to be fast.

TABLE II
CHARGING AND DISCHARGING MEASUREMENT OF THE BATTERY

Variable		Parameter	
Electrolyte Media	Electrolyte Concentration (%)	Charging Slope	Discharging Slope
Gel	10	0.03480	-0.06857
Gel	20	0.00370	-0.00779
Gel	40	0.00285	-0.00450
Liquid	10	0.00351	-0.00677
Liquid	20	0.00353	-0.00569
Liquid	40	0.00258	-0.00456

Table 2 shows the charging and discharging slopes on each battery. The fastest charging slope is in the battery with a liquid electrolyte media concentration of 40% with a value of 0.00258. However, the fastest discharge slope is found in batteries with a liquid electrolyte media concentration of 40% with a value of -0.00456. Meanwhile, the longest charging slope is found in batteries with gel electrolyte media concentration of 10% with a value of 0.03480. However, the longest discharge slope is found in batteries with gel electrolyte media concentration of 10% with a value of -0.06857.

The Steep graph line on the charging process indicates the charging process tends to be fast and a sloping graph line during the charging process shows that the charging process tends to be extended. This also applies to the battery discharging process, where the steep graph line during the discharging process shows the discharging process, which tends to be fast and the sloping graph lines during the discharging process show the discharging process, which tends to be extended [1]. However, the discharging slope's value cannot be used as a reference in this study because there is a potential difference resulting from the battery when galvanostat is applied. Potential differences occur because each battery has different electrolytes used, where the potential value in the galvanostat test ranges from 0.001 volts - 2.715 volts.

IV. CONCLUSION

Cyclic voltammetry and galvanostatic measurements in the performance test of lithium-ion batteries showed that the current generated in cyclic voltammetry measurements resulted in higher values for batteries with liquid electrolyte media compared to gel electrolyte media. Li+ ions are easier to mobilize in batteries with liquid electrolyte media to capture and release Li^+ ions. The current value in the liquid electrolyte media is higher than the current value in the gel electrolyte media. This also applies to the value of concentration; with increasing concentration, the resulting current value also continues to increase. This is due to the increasing number of Li^+ ions. The process of capturing and releasing Li^+ ions in the anode and cathode pores can work optimally. The cyclic voltammetry line graph can be used to find the power and energy values of a lithium-ion battery. The power and energy values are influenced by the electrolyte media, the LiCl concentration, and the lithium ion battery's pressing process. The pressing process that is done incorrectly can affect the power and energy values in the lithium-ion battery.

Galvanostatic measurements show the time it takes to charge and discharge the lithium-ion battery [24]. In this study, the time required for the charging and discharging process on a lithium-ion battery is directly proportional. The electrolyte media influence the time required for charging and discharging. Liquid electrolyte media has a faster time filling and discharging process, whereas gel electrolyte media has a longer time in the filling and discharging process. The time required for the charging and discharging process is affected by the movement of the Li^+ ion. Liquid electrolyte media makes it easier for Li^+ ions to be mobile than gel electrolyte media.

REFERENCES

[1] N. Syarif, D. Rohendi, and M. R. Prayogo, "Preparation of Kerosene Soot Carbon Electrode and Its Application in Lithium Ion Battery," in *2019 6th International Conference on Electric Vehicular Technology (ICEVT)*, Bali, Indonesia, Nov. 2019, pp. 304–309, doi: 10.1109/ICEVT48285.2019.8993970.

[2] M. Contestabile, S. Panero, and B. Scrosati, "A laboratory-scale lithium-ion battery recycling process," *J. Power Sources*, vol. 92, pp. 65–69, 2001.

[3] A. Mishra *et al.*, "Electrode materials for lithium-ion batteries," *Mater. Sci. Energy Technol.*, vol. 1, no. 2, pp. 182–187, Dec. 2018, doi: 10.1016/j.mset.2018.08.001.

[4] H. Chu, Q. Wu, and J. Huang, "Rice husk derived silicon/carbon and silica/carbon nanocomposites as anodic materials for lithium-ion batteries," *Colloids Surf. Physicochem. Eng. Asp.*, vol. 558, pp. 495–503, Dec. 2018, doi: 10.1016/j.colsurfa.2018.09.020.

[5] Yohandri, Zulpadrianto, A. Putra, H. Sanjaya, and J. T. Sri Sumantyo, "A Low-Cost Radar Absorber Based on Palm Shell Active Carbon for Anechoic Chamber," *Int. J. Adv. Sci. Eng. Inf. Technol.*, vol. 9, no. 6, p. 1976, Dec. 2019, doi: 10.18517/ijaseit.9.6.9961.

[6] J. Lee, Y. Wu, and Z. Peng, "Hetero-nanostructured materials for high-power lithium ion batteries," *J. Colloid Interface Sci.*, vol. 529, pp. 505–519, Nov. 2018, doi: 10.1016/j.jcis.2018.06.025.

[7] L. Jörissen and H. Frey, "ENERGY | Energy Storage," in *Encyclopedia of Electrochemical Power Sources*, Elsevier, 2009, pp. 215–231.

[8] N. F. Syabania, N. Syarif, D. Rohendi, M. Wandasari, and W. D. Rengga, "The Light Transmittance and Electrical Conductivity Properties of Gelam Wood Carbon Nanosheet and Its Derivatives," *Indo J Fund Appl Chem*, vol. 4, no. 3, pp. 126–131, 2019.

[9] N. Nitta, F. Wu, J. T. Lee, and G. Yushin, "Li-ion battery materials: present and future," *Mater. Today*, vol. 18, no. 5, pp. 252–264, Jun. 2015, doi: 10.1016/j.mattod.2014.10.040.

[10] N. Syarif, I. A. Tribidasari, and W. Widayanti, "Binder-less activated carbon electrode from gelam wood for use in supercapacitors," *J Electrochem Sci Eng*, vol. 3, no. 2, pp. 37–45, 2014.

[11] T. Kim *et al.*, "Applications of Voltammetry in Lithium Ion Battery Research," *J. Electrochem. Sci. Technol.*, vol. 11, no. 1, pp. 14–25, Feb. 2020, doi: 10.33961/jecst.2019.00619.

[12] S. B. Aziz, T. J. Woo, M. F. Z. Kadir, and H. M. Ahmed, "A conceptual review on polymer electrolytes and ion transport models," *J. Sci. Adv. Mater. Devices*, vol. 3, no. 1, pp. 1–17, Mar. 2018, doi: 10.1016/j.jsamd.2018.01.002.

[13] S. Farahani, "Battery Life Analysis," in *ZigBee Wireless Networks and Transceivers*, Elsevier, 2008, pp. 207–224.

[14] A. Tomaszewska *et al.*, "Lithium-ion battery fast charging: A review," *eTransportation*, vol. 1, p. 100011, Aug. 2019, doi: 10.1016/j.etran.2019.100011.

[15] B. S. Vishnugopi, A. Verma, and P. P. Mukherjee, "Fast Charging of Lithium-ion Batteries via Electrode Engineering," *J. Electrochem. Soc.*, vol. 167, no. 9, p. 090508, Mar. 2020, doi: 10.1149/1945-7111/ab7fb9.

[16] N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart, and J. L. Dempsey, "A Practical Beginner's Guide to Cyclic Voltammetry," *J. Chem. Educ.*, vol. 95, no. 2, pp. 197–206, Feb. 2018, doi: 10.1021/acs.jchemed.7b00361.

[17] A. Ray, A. Roy, S. Saha, and S. Das, "Transition Metal Oxide-Based Nano-materials for Energy Storage Application," in *Science, Technology and Advanced Application of Supercapacitors*, T. Sato, Ed. IntechOpen, 2019.

[18] T. Dobbelaere, P. M. Vereecken, and C. Detavernier, "A USB-controlled potentiostat/galvanostat for thin-film battery characterization," *HardwareX*, vol. 2, pp. 34–49, Oct. 2017, doi: 10.1016/j.ohx.2017.08.001.

[19] C. Liu, Z. G. Neale, and G. Cao, "Understanding electrochemical potentials of cathode materials in rechargeable batteries," *Mater. Today*, vol. 19, no. 2, pp. 109–123, Mar. 2016, doi: 10.1016/j.mattod.2015.10.009.

[20] T.-S. Chen, S.-L. Huang, M.-L. Chen, T.-J. Tsai, and Y.-S. Lin, "Improving Electrochemical Activity in a Semi-V-I Redox Flow Battery by Using a C–TiO_2–Pd Composite Electrode," *J. Nanomater.*, vol. 2019, pp. 1–11, Jan. 2019, doi: 10.1155/2019/7460856.

[21] R. Subramani, Y.-H. Tseng, Y.-L. Lee, C.-C. Chiu, S.-S. Hou, and H. Teng, "High Li^+ transference gel interface between solid-oxide electrolyte and cathode for quasi-solid lithium-ion batteries," *J. Mater. Chem. A*, vol. 7, no. 19, pp. 12244–12252, 2019, doi: 10.1039/C9TA02515D.

[22] J. Menzel, E. Frąckowiak, and K. Fic, "Agar-based aqueous electrolytes for electrochemical capacitors with reduced self-discharge," *Electrochimica Acta*, vol. 332, p. 135435, Feb. 2020, doi: 10.1016/j.electacta.2019.135435.

[23] L. S. Roselin *et al.*, "Recent Advances and Perspectives of Carbon-Based Nanostructures as Anode Materials for Li-ion Batteries," *Materials*, vol. 12, no. 8, p. 1229, Apr. 2019, doi: 10.3390/ma12081229.

[24] R. Suarez-Hernandez, G. Ramos-Sánchez, I. O. Santos-Mendoza, G. Guzmán-González, and I. González, "A Graphical Approach for Identifying the Limiting Processes in Lithium-Ion Battery Cathode Using Electrochemical Impedance Spectroscopy," *J. Electrochem. Soc.*, vol. 167, no. 10, p. 100529, Jun. 2020, doi: 10.1149/1945-7111/ab95c7.

[25] H. Lv, X. Huang, and Y. Liu, "Analysis on pulse charging–discharging strategies for improving capacity retention rates of lithium-ion batteries," *Ionics*, vol. 26, no. 4, pp. 1749–1770, Apr. 2020, doi: 10.1007/s11581-019-03404-8.