

Article

Thermal Studies of Lithium-Ion Cells: Ensuring Safe and Efficient Energy Storage

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Abstract: This work investigated the impact of temperature on the diffusion of lithium ions within cells. To achieve this, electrochemical impedance spectroscopy (EIS) analysis was conducted at various temperatures across three distinct cells. These cells utilized an electrode composed of corn starch meringue and were paired with three different electrolytes. Notably, one electrolyte included an additional 5% of starch. The objective of this study extends beyond merely determining resistance from graphical representations; it also entails performing a kinetic analysis of specific systems, with a particular emphasis on elucidating the significance of the lithium-ion diffusion coefficient as a critical parameter. The cell with 1 M LiPF₆ in the EC/DMC/DEC electrolyte and corn starch-based electrode exhibited the most horizontally oriented Warburg curve, representing the smallest angle.

Keywords: EIS; starch; anode electrode; temperature



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1. Introduction

Lithium-ion (Li-ion) batteries have become an indispensable part of our lives, powering everything from our smartphones to electric vehicles and renewable energy systems. However, as these batteries continue to evolve and push the boundaries of energy density and capacity, managing their thermal behavior has become paramount. Thermal studies of Li-ion cells have gained significant attention in recent years as researchers and engineers work tirelessly to enhance the safety and performance of these power-packed devices.

In recent times, rechargeable lithium-ion batteries (LIBs) have found widespread application across diverse sectors, encompassing everything from compact consumer electronics to large-scale electric vehicles (xEVs) and renewable energy storage systems (ESSs) [1–3]. The persistent concern over “endurance mileage” has been the driving force behind the continuous quest to enhance the energy density of conventional LIBs [4–7]. Simultaneously, alternative battery chemistries “beyond Li-ion” have emerged, including lithium-metal-based batteries, sodium-based batteries, multivalent secondary batteries (such as magnesium-, calcium-, aluminum-, and zinc-based batteries), dual-ion batteries, capacitors, and more [8–11].

However, it is essential to recognize that while LIBs offer remarkable benefits, they also pose significant safety risks when subjected to mechanical, electrical, or thermal abuse. These risks encompass thermal runaway events, which can lead to smoke, fires, and even explosions, posing a direct threat to human lives and property [12,13].

Fortunately, considerable efforts have been dedicated to understanding and enhancing the safety of LIBs at multiple levels, spanning from battery materials to single cells and battery packs [12–15]. Nonetheless, the pace of progress in thermal safety assessments has

often lagged behind the rapid advancements in LIB energy density, often being constrained by a one-dimensional approach [16–20].

To adhere to the principle of “comprehensively addressing every facet of a matter”, it is imperative that we systematically and comprehensively investigate LIB safety. This should involve the integration of diverse testing methods and a holistic understanding of the safety landscape, allowing us to keep pace with the evolving world of LIBs while maintaining the utmost commitment to safety. Lithium-ion batteries are renowned for their high energy density, long cycle life, and fast charge–discharge capabilities. However, they are also susceptible to overheating, which can lead to catastrophic failure, fires, and even explosions. Ensuring safe operation and extending the lifespan of Li-ion cells depend heavily on effective thermal management.

The importance of thermal management cannot be overstated, as it impacts not only the efficiency and longevity of equipment but also safety and environmental concerns. Here, we explore why effective thermal management is paramount in today’s technology-driven world [21–23].

Many industries have strict regulations concerning temperature control. Compliance with these standards is essential to ensure product safety and reliability.

Aging, performance, and safety are the most important features of Li-ion cells, and they are extremely dependent on temperature. So, as a result, for a better battery management system, tracking and having control on the temperature is necessary. As the result, different methods of measuring the temperature have been implemented. The mentioned methods make use of the feature of impedance in electrochemical impedance spectroscopy (EIS) to measure the temperature [24]. As an example, the temperature of a cell can be measured by using surface temperature sensors like thermocouples and thermistors (Figure 1).

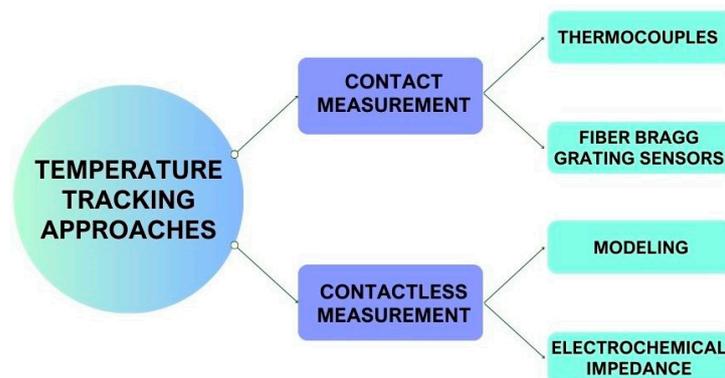


Figure 1. Classification of existing approaches for tracking and controlling the internal temperature of LIBs.

2. The Influence of Temperature on Li-Ion Cells

A lot of temperature-level impacts relate to the chemical reactions taking place in the batteries and also the materials used in the batteries. Pertaining to chemical reactions, the partnership between the rate of chemical reactions and the response temperature follows the Arrhenius equation, and temperature variation can cause a modification in the chemical reaction rate in batteries [25]. Besides chemical reactions, the ionic conductivities of electrodes and electrolytes are likewise affected by temperature levels.

For example, at low temperatures, the ionic conductivity of lithium salt-based electrolytes decreases [26]. In the presence of these issues, the LIBs used in electric vehicles (Evs) and also hybrid electric vehicles (HEVs) can hardly satisfy the assumed 10-year lifespan recommended by the USA Advanced Battery Consortium (USABC) [27]. In the following sections, we will talk about the impact of both low and high temperatures on LIBs.

2.1. Performance of Li-Ion Cells at Low Temperatures

The performance of LIBs will weaken at temperatures below 0 °C [28,29]. Nagasubramanian showed that the power and the power density of Panasonic 18,650 LIBs were 800 W/L and 100 Wh/L at 25 °C, and these values were decreased by 95 to 98 percent at 40 °C [30]. In another report, the state of charge (SOC) of a LIB, which represents the ratio of the capacity to the total available capacity, was decreased by 23% when the operating temperature was lowered from 25 °C to 15 °C [31].

With the complicated product system used in LIBs, performance degradation at low-temperature levels can be dependent on numerous different factors. Initially, the low-temperature level will impact the surface of electrolytes. The viscosity of electrolytes will certainly increase with the reduction in temperature level, which will decrease ionic conductivity. Also, resistance will ultimately rise due to the boost in the impedance of the chemical ions.

2.2. Performance of Li-Ion Cells at High Temperatures

The effects at high temperatures are much more intricate than those at low temperatures. Throughout the operation of the LIBs, because of the heat generated inside batteries, recognizing heat generation is critical in decreasing the impacts of high temperatures on LIBs.

Heat generation is one of the influences which a high temperature has on Li-ion cells. Generally, heat generation within LIBs at a typical temperature level is a phenomenon that happens with the transfer of charge and chemical reactions during charging and discharging [32,33]. The generation of heat happens through reversible reactions or non-reversible reactions. The heat which is generated by a reversible reaction is also called entropic heat; this means that heat is generated based on the reversible changes in entropy during electrochemical reactions [34].

2.3. Generation of Heat in Li-Ion Cells

Generally, heat generation within LIBs at normal temperature levels is connected with cost transfer as well as chain reactions as well as heat release either in the reversible process or the irreparable procedure in LIBs [35]. These reveal feasible reasons for heat generation within LIBs. The heat produced in the reversible procedure, additionally referred to as entropic warmth, stems from the relatively easy-to-fix entropy change throughout electrochemical responses.

2.4. Thermal Runaway in Li-Ion Cells

The possibility of thermal runaway happening increases in the situation that the batteries are produced with defects or are improperly managed. Thermal runaway usually takes place when the battery operates at high temperatures, a situation which provides the requirements for exothermic reactions to occur in operating batteries [36]. These exothermic reactions are able to produce even more heat and subsequently further increase the temperature level inside the batteries [36]. In this situation, the possibility of battery explosions and fire increases. Many manufacturers of digital devices such as Lenovo and Apple have experienced substantial economic losses in the past decades as a result of thermal runaway issues [37,38]. Therefore, recognizing the thermal runaway of LIBs is essential to avoid all types of problems related to high temperatures. In response to this, Finegan et al. [39] first introduced modern in operando technology.

2.5. Flammability of Li-Ion Cells

The electrolyte is one of the most important components in a cell, and the only way to have safer LIBs is to use safer electrolytes. Dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) are examples of the most-used materials in the electrolyte of LIBs because the most popular electrolytes in Li-ion cells are mixtures

containing LiPF_6 and carbonate solvents [40]. Some non-flammable electrolytes are listed in Figure 2, whose use decrease flammability and the possibility of thermal runaway.

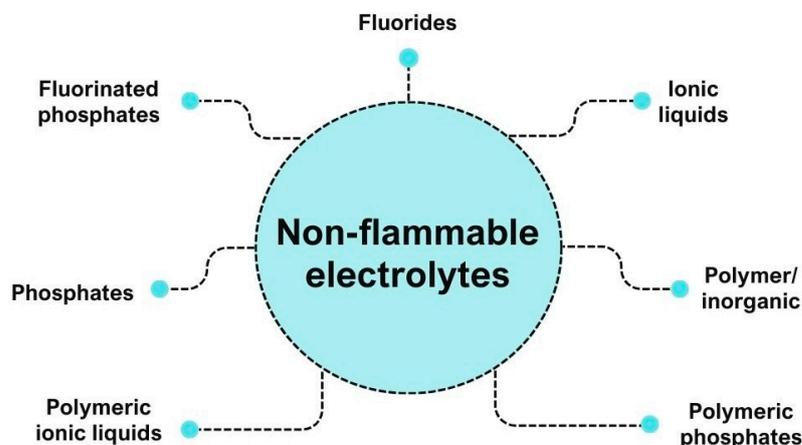


Figure 2. List of the most-known non-flammable liquid electrolytes which can improve the safety of Li-ion batteries [40].

3. Materials and Methods

3.1. Materials

Three cells were prepared in the form of Swagelok: Li | electrolyte | C (Figure 3):

- 1M LiPF_6 (lithium hexafluorophosphate) in EC/DEC (ethylene carbonate: diethyl carbonate—1:1) and corn starch-based electrode—C (after carbonization).
- 1M LiPF_6 (lithium hexafluorophosphate) in EC/DMC/DEC (ethylene carbonate: dimethyl carbonate:diethyl carbonate—1:1:1) and corn starch-based electrode—C (after carbonization).
- 1M LiPF_6 (lithium hexafluorophosphate) in EC/DMC (ethylene carbonate: dimethyl carbonate—1:1) and corn starch in a concentration of 5% and corn starch-based electrode—C (after carbonization).

All samples were prepared in Glove Box. All the products originated from Sigma-Aldrich (Berlin, Germany). Also, a lithium plate was used as a counter electrode.

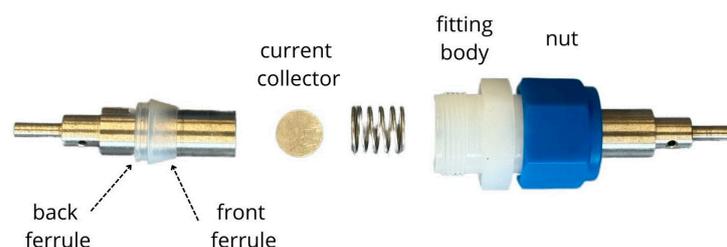


Figure 3. Measuring cell: Swagelok®.

3.2. Methods

Electrochemical impedance spectroscopy (EIS) is a powerful and versatile analytical technique used in the field of electrochemistry. Half-cell impedance measurements were conducted using a GTM750 Potentiostat/Galvanostat/ZRA apparatus (Gamry Instruments, Warminster, PA, USA). The analysis was performed within the frequency range of 100 kHz to 10 mHz, applying an alternating voltage amplitude of 10 mV. Following the measurements, Nyquist plots were obtained in both the real (R) and imaginary ($-iX$) resistance systems. The unit of measurement for both impedances is Ohms.

Key features of electrochemical impedance spectroscopy include the following:

1. **Steady-state Technique.** EIS is a steady-state technique, meaning it operates under conditions of constant amplitude and frequency. This stability allows for the in-depth analysis of electrochemical systems.
2. **Small Signal Analysis.** EIS employs small amplitude signals, ensuring that the system remains in a linear regime. This allows for the extraction of detailed information about the system's behavior without causing significant perturbations.
3. **Frequency Range.** EIS covers a wide frequency range, typically from less than 1 Hz to more than 1 MHz. This broad spectrum enables the investigation of processes occurring at different time scales.
4. **Instrumentation.** The technique utilizes specialized instrumentation known as a potentiostat/galvanostat, which controls the applied potential or current during the experiment. This ensures precise control over the electrochemical conditions.

Applications of EIS are diverse and include the following (Figure 4):

- **Battery Research:** EIS is crucial for characterizing the electrochemical behavior of batteries, aiding in the optimization of battery materials and performance.
- **Corrosion Studies:** It is widely used to investigate the corrosion processes in metals and alloys, providing insights into protective coatings and corrosion inhibitors.
- **Biosensors:** EIS is employed in the development of biosensors for detecting specific biomolecules, offering high sensitivity and selectivity.
- **Fuel Cells:** Researchers use EIS to study and improve the efficiency of fuel cells by understanding the electrochemical processes involved.

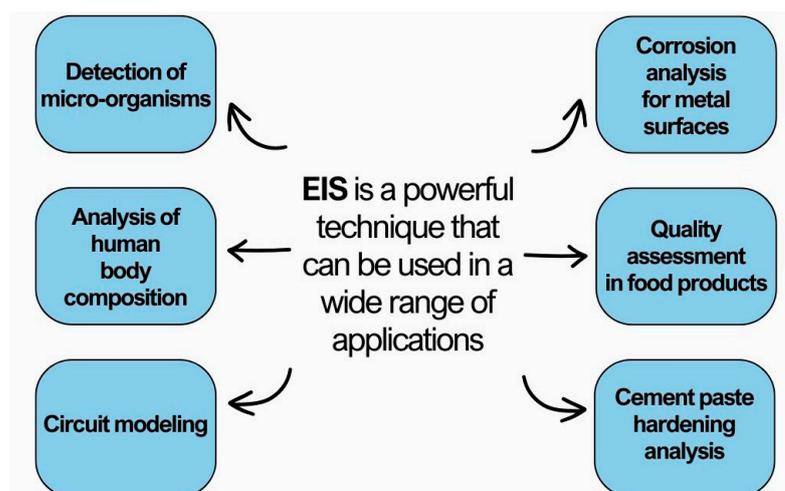


Figure 4. Applications of Electrical Impedance Spectroscopy (EIS) [41].

4. Results

4.1. Investigation of Electrochemical Impedance Spectroscopy with Consideration of Temperature Variations for the Studied Systems

To investigate the impact of temperature on electrochemical impedance spectroscopy (EIS), measurements were conducted at various temperatures ranging from 25 °C to 50 °C. Additionally, the thermal stability of the electrolyte was assessed using the Wamed KBC thermal chamber (18 W) (WAMED Medical Equipment Factory S.S.P, 03-310 Warszawa, Poland). As the temperature increased, both the ion migration speed and the reaction rate accelerated, leading to a decrease in $R\Omega$. This investigation was motivated by the flammability of Li-ion batteries, aiming to evaluate the thermal and electrochemical performance of cells and explore their potential enhancement through the addition of starch, leveraging its non-Newtonian properties (Figure 5a–c). However, despite the excellent stability of the electrolyte, there was no significant reduction in resistance as the temperature increased. This phenomenon can be attributed to the temperature affecting the ion charge transfer process at the electrode/electrolyte interface, leading to a notable decrease in R_{ct} with rising

temperatures [42]. Specifically, the sluggish kinetics resulting from this effect can lead to poor performance at low temperatures [43].

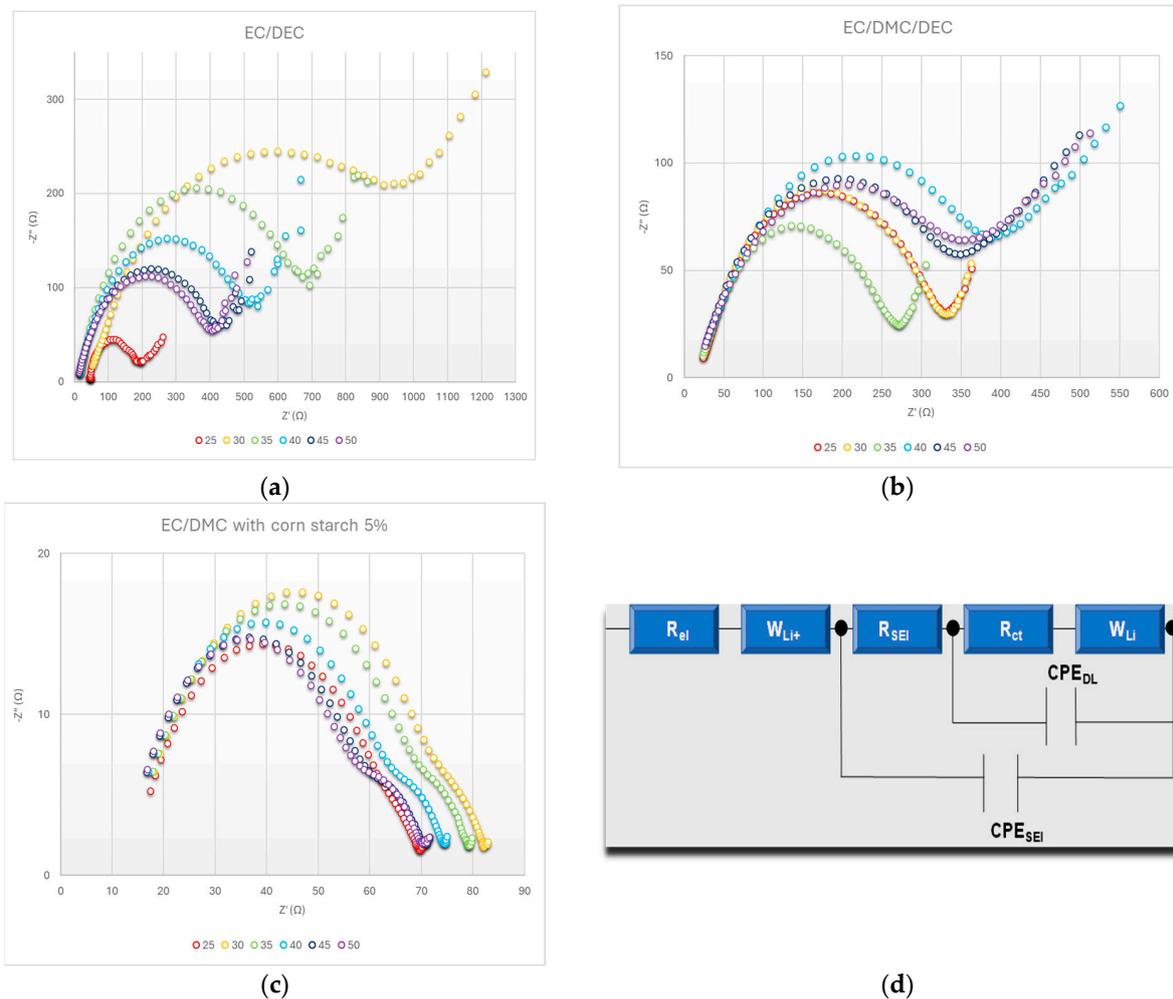


Figure 5. (a) Nyquist plots of cell LiPF_6 in EC/DEC as electrolyte and corn starch-based electrode under 25, 30, 35, 40, 45, and 50 °C; (b) Nyquist plots of cell LiPF_6 in EC/DMC/DEC as electrolyte and corn starch-based electrode under 25, 30, 35, 40, 45, and 50 °C; (c) Nyquist plots of cell LiPF_6 in EC/DMC + corn starch 5% as electrolyte and corn starch-based electrode under 25, 30, 35, 40, 45, and 50 °C; (d) the equivalent circuit.

The equivalent circuit for the anode material and the electrolyte used in lithium-ion cells contains elements such as CPE_{DL} —double layer capacitance, CPE_{SEI} —SEI layer capacitance, R_{ct} —charge transfer resistance and the resistance of the passive layer of the particle interface, R_{el} —the resistance of the electrolyte, and W_{Li^+} —the Warburg impedance associated with the diffusion of Li^+ (Figure 5d). The linear section of the Nyquist plot represents the Warburg line that is initiated because of the diffusion of lithium ions into the active material. The resistance becomes lower due to the transfer of the charge. The system becomes more stable when more SEI is produced. SEI mostly decreases the possibility of corrosion on the electrode and keeps its great cyclic properties. Beside these advantages, SEI has also negative effects; they can cause significant anisotropic diffusion on the surface of electrode. As a result, we have low efficiency in the battery.

4.2. Thermodynamic Modeling of the Diffusion Process

Thermodynamic modeling of the diffusion process involves applying principles from thermodynamics to analyze and predict the behavior of diffusing species in various systems.

In thermodynamic modeling of diffusion, key concepts such as entropy, free energy, and temperature are employed to understand the driving forces and constraints influencing the diffusion process. Thermodynamics relates to the entropy changes associated with the diffusion process. As particles move from regions of higher concentration to lower concentration, the system tends to increase its overall entropy. The analysis of free energy changes provides insights into the spontaneity and feasibility of diffusion. Thermodynamic modeling allows for the calculation of free energy changes associated with the diffusion process, helping to predict whether diffusion will occur under specific conditions. Temperature is a critical parameter in thermodynamic modeling. By considering how temperature influences the thermodynamic parameters involved in diffusion, researchers can predict how diffusion rates change with temperature variations.

The electrochemical cell feedback is pseudo-linear in which a phase shift is acquired while the existing response to a sinusoidal capacity is a sinusoid at the used frequency. Therefore, the excitation signal is presented as a function of time, as received in Equation (1) [44]:

$$E_t = E_0 \cdot \sin(\omega t) \quad (1)$$

where E_t is the potential at time t , E_0 is the amplitude of the signal, and ω is the radial frequency.

The correlation between the radial frequency (ω) and the applied frequency (f) is calculated by Equation (2) [45]:

$$\omega = 2 \cdot \pi \cdot f \quad (2)$$

In a linear system, the signal is shifted in phase (Φ) and has a different amplitude than I_0 [46]:

$$I_t = I_0 \cdot \sin(\omega t + \Phi) \quad (3)$$

As the result, the total impedance can be obtained from Equation (4) [47]:

$$Z = \frac{E}{I} = Z_0 \exp(i\Phi) = Z_0(\cos\Phi + i\sin\Phi) \quad (4)$$

where Z , E , I , ω , as well as Φ impedance, potential, current, frequency, and phase change in between E and I , specifically. The insusceptibility is expressed in regard to the magnitude, Z_0 , and the phase change, Φ .

During electrochemical reactions in electrodes, the spread of Li on the surface of electrodes occurs in different levels and amounts. This process indicates the presence and density of Li-ions which results in Li-ion diffusion. This is one of the factors that has a very important role in the kinetic process of electrode materials, because diffusion is a factor for determining reaction velocity in electrode materials and, as a result, it has influence on the performance of the electrode.

The diffusion procedure in the electrolyte has an impact, inter alia, on minimal energy and power density; therefore, restricting the present density results in a diffusion-limited C-rate (DLC).

To identify the diffusion coefficient D_{Li+} ($\text{cm}^2 \text{s}^{-1}$), the Warburg area in the Nyquist plots is thought of as utilizing Formula (5) [48]:

$$D_{Li+} = \frac{R^2 T^2}{2A^2 \cdot n^4 \cdot F^4 \cdot c^2 \cdot \sigma^2} \quad (5)$$

where the R refers to a gas constant equal to $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T refers to the standard temperature (298 K), A refers to the active electrode surface (1.54 cm^2), n refers to the number of the electrons taking part in the oxidation process, F refers to the Faraday constant ($96,500 \text{ C mol}^{-1}$), c refers to the molar concentration of lithium ions in LiPF_6 electrolyte ($0.001 \text{ mol} \cdot \text{cm}^{-3}$), and σ refers to the diffusion constant from the linear regression equation ($\Omega \text{ s}^{-1/2}$) [49]:

$$Z' = R_D + R_L + \sigma \omega^{-1/2} \quad (6)$$

In addition, to achieve sigma σ , the plots of Z' and Z'' versus $\omega^{-1/2}$, for a variety of diffusion resistances, were developed as well as the slope amounting to σ .

According to Fick's law, motion occurs on a surface area vertical to the direction of particle movement. Hence, for the calculations, the electrode surface was made use of. Nonetheless, when considering the diffusive movement of the ions with the porous framework of the electrode product, it would be better suited for us to make use of the wager SSA. This is due to the fact that this location defines the environment in which this mass transportation occurs.

When interpreting the relationship between the diffusion coefficient and the permeable framework or the growth of this area, and when it comes to bigger pore sizes (meso- and also macropores), diffusion is a lot more effective. It is opposed to the microporous framework, in which the area where Li-ions can diffuse is much smaller-sized.

This suggests that the mesopores present in the samples obtained in this study facilitate easier mass transportation by allowing for this phenomenon to occur. Generally, the diffusion rate of ion transportation is hindered by resistance. It is important to note that the critical area is always the active surface area (ASA). However, due to the challenging methods for its determination, the specific surface area (SSA) is typically utilized. Regarding the ASA, it encompasses the portion of the electrode surface directly involved in electrochemical processes, primarily Li-ion sorption. Since various factors are indirectly considered, the ASA may not always equate to the SSA. It is crucial to recognize that the entire surface may not contribute to mass transfer. Furthermore, this implies that the sorption capacity of the adsorbent material does not uniformly correspond to 1 g cm² of the sample. Additionally, the ratio of pore size to ion size also greatly influences this phenomenon.

So, to obtain the activation energy of diffusion ($E_D^\#$) [50], the following was utilized:

$$\ln \frac{A_w}{T} = \beta - \frac{E_D^\#}{2R} \cdot \frac{1}{T} \quad (7)$$

In the next step, the Nernst–Einstein relation was utilized to figure out the ionic conductivity of lithium ions (σ_{Li^+}) in the Warburg region [51]:

$$\sigma_{Li^+} = \frac{c \cdot D_{Li^+} \cdot n^2 \cdot F^2}{RT} \quad (8)$$

Furthermore, to attain the pre-exponential element A , the following formula was proposed [42]:

$$\sigma_{Li^+} = A \cdot \exp\left(\frac{-E_D^\#}{k_B T}\right) \quad (9)$$

where k_B is the Boltzmann constant. Subsequently, the Arrhenius formula was used to compute the value of k [52]:

$$k = A \cdot \exp\left(\frac{-E_D^\#}{RT}\right) \quad (10)$$

To obtain the Gibbs function, the Eyring–Polanyi equation was used, where h is the Planck constant [53]:

$$k = \frac{k_b \cdot T}{h} \cdot \exp\left(-\frac{\Delta G}{RT}\right) \quad (11)$$

Ionic conductivity is a considerable criterion in regard to examining the effectiveness of the solution utilized. It is used not only in electrochemistry but also in environmental chemistry and biochemistry. It needs to be kept in mind that, among other specifications, the ionic conductivity in batteries, electro dialysis devices, as well as supercapacitors changes with the change in concentration and temperature, while the solvent structure typically stays the same or is not taken into account. Consequently, to boost the functioning of electrochemical systems, tests of electrolyte conductivity as a function of temperature and focus ought to be executed.

4.3. The Relationship between Diffusion and Temperature Dependence

The interplay between diffusion and temperature reveals a significant dependence, as temperature plays a crucial role in influencing the rate and extent of diffusion processes. Changes in temperature can directly impact the kinetic energy of particles within a substance, affecting their mobility and propensity to move from regions of higher concentration to lower concentration. In essence, the diffusion rate tends to increase with elevated temperatures due to the heightened energy levels of particles, promoting more frequent collisions and facilitating the overall dispersal of substances. Understanding this temperature-dependent relationship is fundamental in various scientific and industrial contexts, providing insights into diffusion phenomena and aiding in the optimization of processes where diffusion is a key factor. Firstly, measurements were taken at room temperature both before and after charging. Here, we examined the impact of the safety test on resistance ratios. The highest diffusion coefficient ratio (Table 1) was observed for EC/DMC/DEC. It is important to note that diffusion coefficients are significantly higher for commercial carbon products and depend on the synthesis technique. This observation also indicates that satisfactory results were achieved.

Table 1. Constant δ , diffusion coefficient, and ionic conductivity for cell LiPF₆ in EC/DMC/DEC as electrolyte and corn starch-based electrode after charging at the following temperatures: 25, 30, 35, 40, 45, and 50 °C.

Sample	Temperature (°C)	δ ($\Omega \text{ s}^{-0.5}$)	D_{Li^+} ($\text{cm}^2 \text{ s}^{-1}$)	σ_{Li^+} (S cm^{-1})
EC/DMC/DEC	25	2.41	6.73×10^{-8}	1.94×10^{-5}
	30	2.33	8.04×10^{-8}	3.35×10^{-5}
	35	2.12	1.32×10^{-7}	3.72×10^{-5}
	40	2.03	1.62×10^{-7}	4.78×10^{-5}
	45	2.01	1.73×10^{-7}	5.10×10^{-5}
	50	1.79	2.38×10^{-7}	6.35×10^{-5}

As it is shown in Table 1, to evaluate the behavior of lithium ions at different temperatures during loading, Nyquist plots were analyzed after information deconvolution in the temperature level range of 25–50 °C at every 5 °C. Among all that were analyzed, EC/DMC/DEC was picked as one of the most electrochemically active. Thus, only this product continued to be evaluated. Then, the activation energies of the kinetic control procedures were established.

The diffusion coefficient of lithium ions and ionic conductivity were identified. On this basis, thermodynamic specifications (including the Gibbs function, entropy, enthalpy, and the balance constant) and kinetic parameters (reaction rate constant, activation energy) for lithium-ion intercalation were estimated (Figure 6a–f).

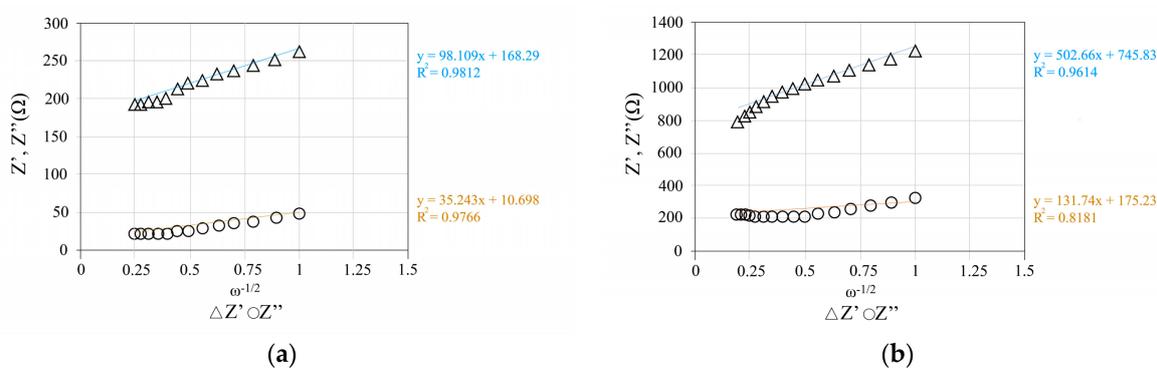


Figure 6. Cont.

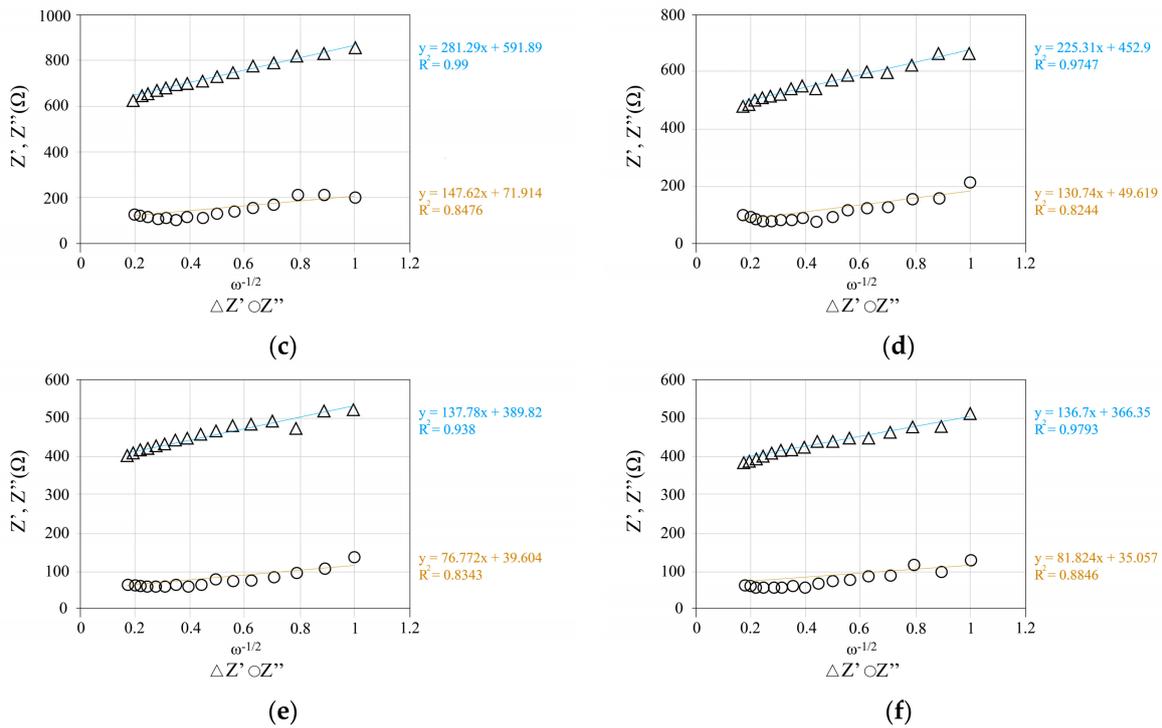


Figure 6. Graphical interpretation of diffusion coefficient for cell LiPF_6 in EC/DEC as electrolyte and starch-based electrode: (a) 25 °C; (b) 30 °C; (c) 35 °C; (d) 40 °C; (e) 45 °C; (f) 50 °C.

Based on the data obtained during and after the experiments as well as the graphs drawn using these data, it was observed that the cell with EC/DMC/DEC (Figure 7a–f) exhibits lower impedance and resistance compared to the cells with other electrodes, such as EC/DMC and 5% starch (Figure 7c), and the cell with EC/DEC (Figure 7a). This characteristic makes the cell with EC/DMC/DEC more reliable and an intriguing option for use in various industries.

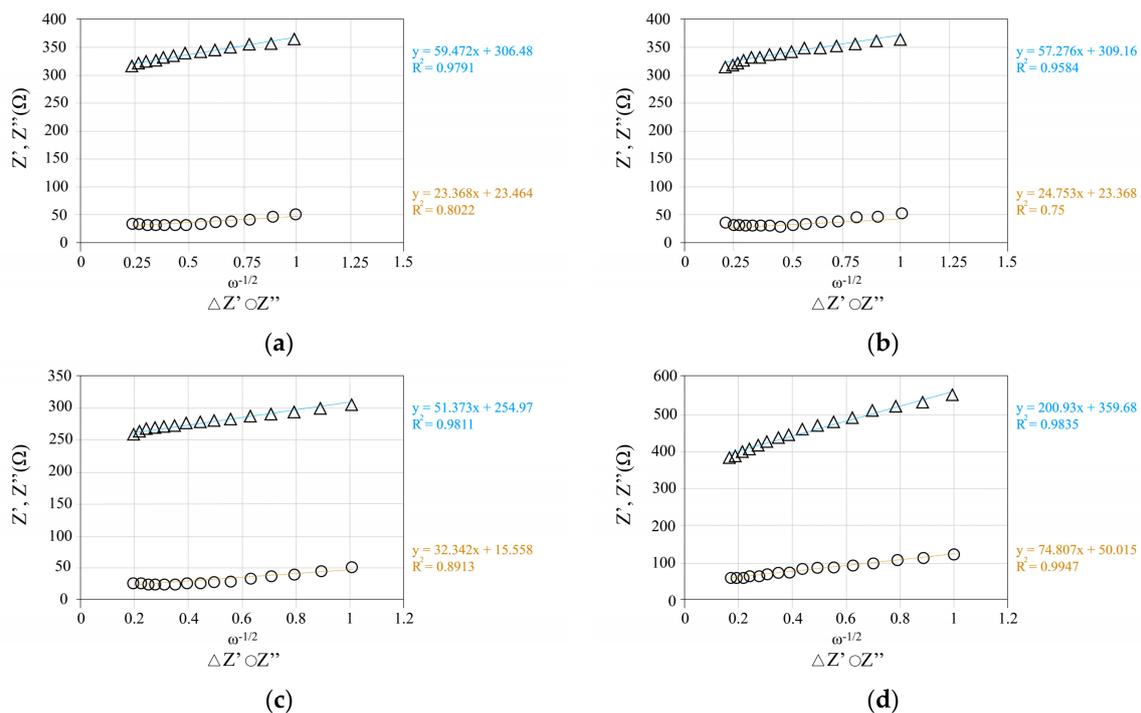


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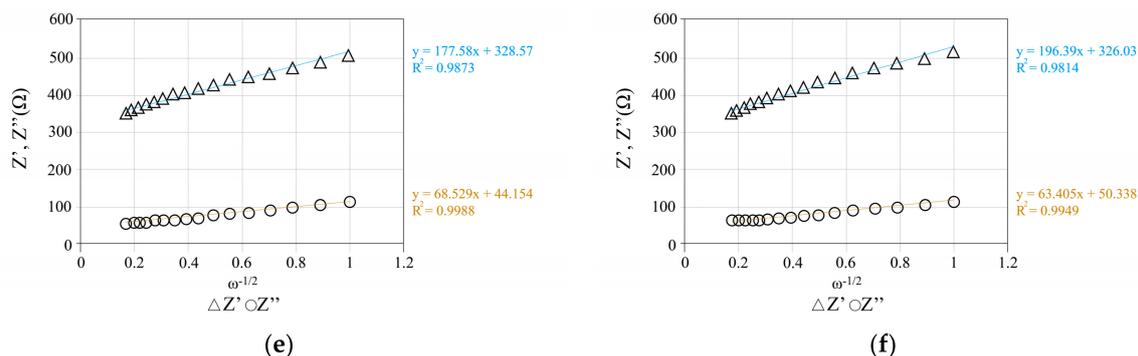


Figure 7. Graphical interpretation of diffusion coefficient cell LiPF₆ in EC/DEC/DMC as electrolyte and starch-based electrode: (a) 25 °C; (b) 30 °C; (c) 35 °C; (d) 40 °C; (e) 45 °C; (f) 50 °C.

Additionally, according to Table 1, it is already proven that temperature has an inverse relationship with resistance. Therefore, by increasing the temperature, lower resistance will be observed, leading to a decrease in SEI layer thickness. One of the notable features of the cell with EC/DMC/DEC is its connection with temperature and resistance, making it more suitable for use in high-temperature ranges. Simultaneously, some electrons will relocate from different atoms and surroundings to the Li-ions, a process known as charge transfer. Charge transfer has a direct connection with temperature, with higher values observed as the temperature increases. In conclusion, the transfer of charge does not stop or reduce at high temperatures, rendering it an advantage for the cell with EC/DMC/DEC.

However, there are some restrictive factors and problems that may affect the values and specifications of impedance during experiments, such as adjusting the separators properly by paying attention to the electrodes in the form of Swagelok. Additionally, using the appropriate electrolyte is crucial for proper electrode wettability.

As indicated in Table 2, it is evident that higher temperatures result in an increased diffusion process [12], leading to an augmentation in the thickness of the SEI layer. Additionally, based on information available in the literature, the aging phenomenon, thermal runaway, and the overall generation of heat pose significant disadvantages for Li-ion cells. Understanding the cell's behavior at lower temperatures is comparatively simpler than at higher temperatures. Given that these factors are crucial for safety and the overall life cycle of the cell, it becomes essential to consider such phenomena across different temperature ranges.

Table 2. Deconvolution of spectra at temperatures of 25–50 °C for EC/DMC/DEC.

Temperature (°C)	R _{el} (Ω)	R _{SEI} (Ω)	R _{ct} (Ω)	W _{Li+}
25	20.68	142.9	34.44 · × 10 ⁻¹	1.96 · × 10 ⁻³
30	20.37	125.30	38.81 · × 10 ⁻¹	8.13 · × 10 ⁻³
35	19.30	86.86	18.30 · × 10 ⁻¹	3.42 · × 10 ⁻³
40	18.01	79.13	1.28 · × 10 ²	4.43 · × 10 ⁻³
45	17.20	73.46	8.17 · × 10 ²	3.27 · × 10 ⁻³
50	12.92	56.07	7.79 · × 10 ²	6.53 · × 10 ⁻³

Table 3 provides insight into the cell's behavior, ongoing processes, and observed phenomena. In the heat generation process, most reactions are irreversible, except for electrochemical reactions, which are reversible.

All observations regarding the cell's behavior in the temperature range of 20 to 800 °C are detailed in Table 3, categorized into different temperature ranges based on when distinct ongoing processes in the cell are observed. The table is divided into 10 temperature ranges, each specifying a particular process and behavior that is observed.

Table 3. Thermal stages for LIB according to different temperatures of the cell work [54].

Temperature (°C)	Observation
20–80	Heat-Wait Seek in ARC (Accelerating Rate Calorimetry)
60–110	SEI decomposition
60–140	Self-discharge of the cathode
70–110	Anode reaction consumption of Li in the anode
120–230	Anode reaction consumption of the active material
120–150	Melting of the separator
150–220	Micro inner short circuit; melting of the polyethylene separator
230–255	Separator breakup
230–800	Quick internal short circuit
240–800 and above	Decomposition of the NMC cathode
250–800 and above	An electrolyte decomposition
250–800 and above	A binder decomposition
450–800 and above	The temperature rises with the cooling of the ARC

To obtain the activation energies of the electrolyte conduction process ($E_{el}^{\#}$) and the SEI layer ($E_{SEI}^{\#}$), plots $\ln R^{-1} = f(T^{-1})$ were created. The slopes multiplied by the gas constant R indicate the activation energies (Arrhenius equation).

Figures 6–8 show the graphic interpretation of the determination of the diffusion coefficient for cell LiPF_6 in EC/DEC, EC/DMC/DEC, and EC/DMC with 5% starch as the electrolyte and starch-based electrode.

In electrode materials, there are two types of kinetic processes during the charging and discharging of Li-ion cells:

- Addition and removal of Li-ions: This involves the incorporation and extraction of Li-ions within the electrode material during the charge and discharge cycles.
- Transfer of charge during the addition and removal of Li-ion cells resulting from the reduction and oxidation of electrode materials: This refers to the movement of charge associated with the reduction and oxidation reactions occurring in electrode materials during the electrochemical process.

During the electrochemical reaction in electrodes, the distribution of Li-ions on the surface and inside the electrodes differs. This indicates variations in Li-ion concentration within the cell, leading to Li-ion diffusion. The diffusion of Li-ions plays a crucial role, significantly influencing the kinetic processes in electrode materials [55,56]. Both anode and cathode materials consist of a mixture of ionic and electronic conductors.

The enhancement of both types of conduction can be achieved through different methods. Electronic conduction can be improved by enhancing electronic conductivity, often achieved through technical advancements such as carbon coating and the addition of conduction additives [57]. In the case of ionic conduction, ionic conductivity stands out as the most critical factor. Improving ionic conductivity is challenging, as the transfer of ions in ionic conductors relies entirely on material composition and structure. Although the rate of capability can be enhanced by reducing particle size in electrode materials and shortening the Li-ion transport route [57], this might lead to a sudden increase in the specific surface area of electrode materials. All these processes may pose challenges related to the stability of the interface and surface.

Moreover, it is evident that ionic conductivity is a crucial factor in Li-ion cells. Since ionic conductivity is directly related to diffusion, an increase in ionic conductivity, especially at higher diffusion values, becomes a significant factor influencing the intercalation of Li-ions, charge transfers during the charge and discharge processes, and the formation of the Solid Electrolyte Interface (SEI) layer.

Thermal studies of Li-ion cells involve a deep exploration of their behavior under various operating conditions. Researchers use a range of techniques and tools, including thermal imaging, calorimetry, and mathematical modeling, to gain insights into how these batteries respond to temperature fluctuations, charge–discharge cycles, and abuse conditions.

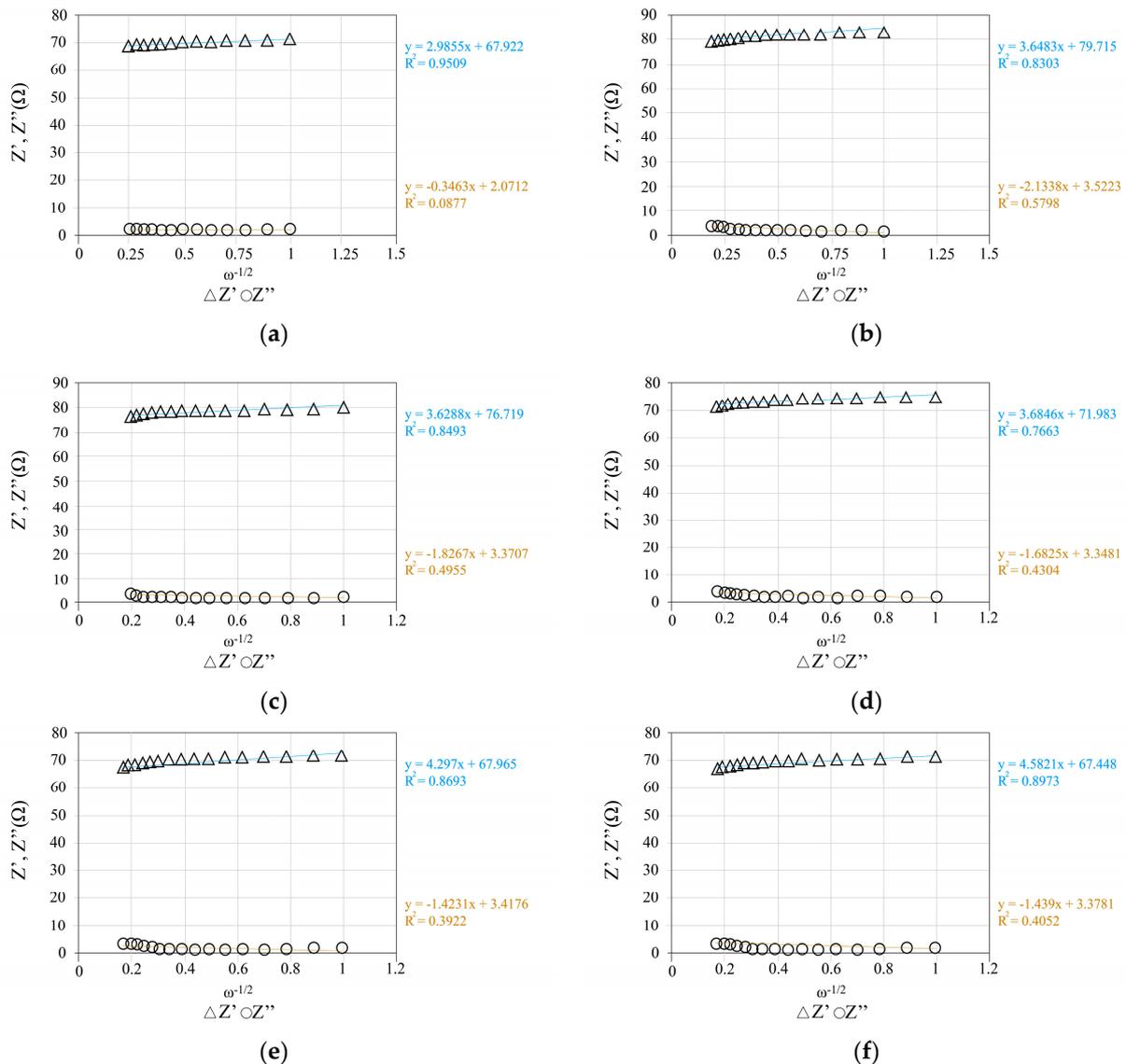


Figure 8. Graphical interpretation of diffusion coefficient for cell LiPF₆ in EC/DMC with 5% starch as electrolyte and starch-based electrode: (a) 25 °C; (b) 30 °C; (c) 35 °C; (d) 40 °C; (e) 45 °C; (f) 50 °C.

In various fields of science and engineering, the study of thermal behavior holds a pivotal role. Understanding how temperature changes affect materials, systems, and processes is crucial for optimizing performance, ensuring safety, and advancing technology. Here, we delve into the significance of comprehending thermal behavior and the tools and methods employed to gain insights into this complex phenomenon.

4.4. Challenges and Future Directions in Thermal Studies of Lithium-ion Batteries (LiBs)

While significant progress has been made in understanding the thermal behavior of Li-ion cells, challenges remain. Achieving even greater safety and performance gains requires continued research into advanced materials, cooling techniques, and thermal management strategies.

Thermal studies of lithium-ion batteries (LiBs) have made significant strides in enhancing the safety, performance, and longevity of these essential energy storage devices. However, as LiB technology continues to evolve and diversify, several challenges and promising future directions emerge in the realm of thermal research:

- **Complex Battery Designs**—the ever-evolving landscape of LiB designs, including pouch, cylindrical, and prismatic configurations, presents challenges in standardizing thermal studies and ensuring consistent results across diverse formats.
- **Multi-Physics Interaction**—LiBs are subject to complex interplays of electrical, thermal, and mechanical phenomena. Understanding these multi-physics interactions and their effects on thermal behavior remains a significant challenge.
- **High-Energy-Density Cells**—next-generation LiBs aim for even higher energy density, which can exacerbate thermal management challenges. Developing efficient cooling and thermal mitigation strategies becomes increasingly critical.
- **Safety Concerns**—as LiBs push the boundaries of energy density, safety concerns related to thermal runaway events demand continuous research. Mitigating these risks through innovative thermal management solutions is an ongoing challenge.
- **Aging and Degradation**—thermal studies must account for the aging and degradation of LiBs over time. Identifying and quantifying the thermal effects on degradation mechanisms is crucial for extending battery lifespans.

Exploring advanced materials for LiB components, such as improved thermal conductive separators and electrode materials, can contribute to better thermal performance.

4.5. Risks and Safety Concerns with Lithium-ion Batteries

While lithium-ion batteries offer numerous advantages over various rechargeable counterparts, they do have specific drawbacks, particularly in terms of safety and security, despite their technological potential. Li-ion batteries have notable limitations, primarily related to safety concerns associated with high voltages that can lead to overheating, thermal runaway, and even combustion. These issues have raised substantial alarms, including the grounding of the Boeing 787 fleet following reports of in-flight battery fires. Due to these battery-related risks, several shipping companies have refrained from transporting batteries in bulk via air, and the high cost of Li-ion batteries, approximately 40% more than nickel–cadmium (Ni-Cd) batteries, presents an additional obstacle to widespread adoption. Addressing these challenges constitutes a crucial component of ongoing technical research.

Overcharging, excessive discharging, or internal short-circuits within a lithium-ion cell can result in undesirable side effects, including exothermic chemical reactions, as previously detailed. Internal short circuits arise when electrodes within the same cell make contact, creating conditions conducive to exothermic reactions. Overcharging, on the other hand, occurs when electricity is forcibly driven through a cell that has already reached its specific capacity [14]. Numerous factors can contribute to battery overcharging, with one common issue being cell mismatch. This situation can occur when the control system fails to effectively monitor voltage levels across the battery pack. To illustrate, consider the $\text{LiCoO}_2/\text{LiPF}_6\text{-EC-DEC}/\text{C}$ (graphite) system: the battery overcharging process typically commences during the normal charging phase (2.8–4.2 V). In each cell, lithium ions are extracted from the cathode material (LiCoO_2) and migrate toward the anode material (graphite). To maintain high reversibility in lithium intercalation and deintercalation, the voltage is carefully regulated within a range that aligns with the reversible changes in the electrode's crystal structure and phases. Only 50% of the lithium is extracted from the cathode to ensure the stability of the crystal structure and capacitance reversibility [15]. Operating within this voltage range (2.8–4.2 V) during charging and discharging results in minimal volume changes within the cathode material and safeguards the LiCoO_2 crystal structure, ensuring safe battery operation.

However, when one of the cells starts with a higher charge percentage before charging and the control system malfunctions, the voltage can eventually surpass the designated maximum value (around 4.2 V). Overcharging ensues, causing excessive lithium deintercalation from the cathode material until almost all lithium is removed. Consequently, irreversible phase changes occur, leading to the disintegration of the LiCoO_2 crystal structure, evidenced by cobalt deposition on the anode's surface. Additionally, cathode decomposition generates oxygen gas, and excess Li^+ cations on the anode give rise to dendritic lithium

formation. These lithium dendrites can pierce the separator, causing electrode contact and resulting in a short circuit.

5. Conclusions

Thermal studies of lithium-ion cells are at the forefront of battery research, playing a vital role in ensuring the safety and efficiency of these power sources. As Li-ion batteries continue to power our ever-evolving world, ongoing research into their thermal behavior will be instrumental in harnessing their full potential while minimizing risks. The insights gained from these studies are not only shaping the future of energy storage but also contributing to the broader goal of sustainable and reliable power solutions for a rapidly changing world.

Researching the high-temperature thermal properties of LiPF₆/EC/DEC, LiPF₆/EC/DMC/DEC and LiPF₆/EC/DMC with 5% corn starch revealed that in the 1 M LiPF₆/EC + DMC + EMC electrolyte, LiPF₆ may react with EC, DMC, and EMC individually. Furthermore, it was observed that LiPF₆ significantly influences thermal behavior, resulting in increased heat generation and lower onset temperature.

Graphs derived from our experimental data showed that the cell with 1M LiPF₆ in EC/DMC/DEC exhibited the highest electrochemical activity. This battery also demonstrated the lowest resistance, with diffusion coefficients surpassing those of other cells.

The most horizontally oriented Warburg curve was associated with the LiPF₆ cell in EC/DMC/DEC electrolyte and corn starch-based electrode (the smallest angle), indicating lower ionic conductivity compared to other experimented cells. Consequently, this cell exhibited lower ionic conductivity, making it more beneficial and a superior battery.

Furthermore, the LiPF₆ cell in EC/DMC/DEC, which had the lowest resistance among the cells studied, was compared to other Li-ion cells with different electrolytes, including the EC/DMC/DEC cell. Higher conductivity helps to minimize internal resistance within the battery. High conductivity electrolytes can help maintain battery performance even at low temperatures. This is crucial for applications like electric vehicles, where batteries need to operate efficiently in various environmental conditions.

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References

1. Tarascon, J.M.; Armand, M. Issues and challenges facing rechargeable lithium batteries. *Nature* **2001**, *414*, 359–367. [[CrossRef](#)]
2. Lewis, G.N. The potential of lithium electrode. *J. Am. Chem. Soc.* **1913**, *192*, 1126–1127. [[CrossRef](#)]
3. Whittingham, M.S. Electrical Energy Storage and Intercalation Chemistry. *Science* **1976**, *192*, 1126–1127. [[CrossRef](#)]
4. Touzain, P.; Ry, R. Insertion Compounds of Graphite with Improved Performances and Electrochemical Applications of Those Compounds. U.S. Patent 4,584,252, 22 April 1986.
5. Winter, M.; Besenhard, J.O.; Spahr, M.E.; Novak, P. Insertion electrode materials for rechargeable lithium batteries. *Adv. Mater.* **1999**, *10*, 725–763. [[CrossRef](#)]
6. Mizushima, K.J.P.C.; Jones, P.C.; Wiseman, P.J.; Goodenough, J.B. Li_xCoO₂ (0 < x < 1): A new cathode material for batteries of high energy density. *Mater. Res. Bull.* **1980**, *15*, 783–789.
7. Tozawa, K.; Tozawa, T.N. Lithium Ion Rechargeable battery. *Prog. Batter. Sol. Cells* **1990**, *9*, 209.
8. Ozawa, K. Lithium-ion rechargeable batteries with LiCoO₂ and carbon electrodes: The LiCoO₂/C system. *Solid State Ion.* **1994**, *69*, 212–221. [[CrossRef](#)]
9. Ehrlich, G.M. Lithium-ion batteries. In *Handbook of Batteries*; McGraw Hill: New York, NY, USA, 2002; pp. 35–53.
10. Li, D.; Zhou, H. Two-phase transition of Li-intercalation compounds in Li-ion batteries. *Mater. Today* **2014**, *17*, 451–463. [[CrossRef](#)]

11. Dong, X.; Chen, L.; Liu, J.; Haller, S.; Wang, Y.; Xia, Y. Environmentally-friendly aqueous Li (or Na)-ion battery with fast electrode kinetics and super-long life. *Sci. Adv.* **2016**, *2*, e1501038. [[CrossRef](#)]
12. Montanino, M.; Passerini, S.; Appetecchi, G.B. Electrolytes for rechargeable lithium batteries. In *Rechargeable Lithium Batteries*; Elsevier: Amsterdam, The Netherlands, 2015; pp. 73–116. [[CrossRef](#)]
13. Mishra, A.; Mehta, A.; Basu, S.; Malode, S.J.; Shetti, N.P.; Shukla, S.S.; Nadagouda, M.N.; Aminabhavi, T.M. Electrode materials for lithium-ion batteries. *Mater. Sci. Energy Technol.* **2018**, *1*, 182–187. [[CrossRef](#)]
14. Gnanaraj, J.S.; Zinigrad, E.; Asraf, L.; Gottlieb, H.E.; Sprecher, M.; Schmidt, M.; Geissler, W.; Aurbach, D. A detailed investigation of the thermal reactions of LiPF₆ solution in organic carbonates using arc and dsc. *J. Electrochem. Soc.* **2003**, *150*, A1533. [[CrossRef](#)]
15. Ouyang, D.; Chen, M.; Liu, J.; Wei, R.; Weng, J.; Wang, J. Investigation of a commercial lithium-ion battery under overcharge/over-discharge failure conditions. *RSC Adv.* **2018**, *8*, 33414–33424. [[CrossRef](#)] [[PubMed](#)]
16. Chen, Y.; Kang, Y.; Zhao, Y.; Wang, L.; Liu, J.; Li, Y.; Liang, Z.; He, X.; Li, X.; Tavajohi, N.; et al. A review of lithium-ion battery safety concerns: The issues, strategies, and testing standards. *J. Energy Chem.* **2021**, *59*, 83–99. [[CrossRef](#)]
17. Aravindan, V.; Gnanaraj, J.; Lee, Y.-S.; Madhavi, S. LiMnPO₄—A next generation cathode material for lithium-ion batteries. *J. Mater. Chem. A* **2013**, *1*, 3518–3539. [[CrossRef](#)]
18. Shaju, K.M.; Subba Rao, G.V.; Chowdari, B.V.R. Performance of layered Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ as cathode for Li-ion batteries. *Electrochim. Acta* **2002**, *48*, 145–151. [[CrossRef](#)]
19. Akimoto, J.; Gotoh, Y.; Oosawa, Y. Synthesis and Structure Refinement of LiCoO₂ Single Crystals. *J. Solid State Chem.* **1998**, *141*, 298–302. [[CrossRef](#)]
20. Madhu, C.; Garrett, J.; Manivannan, V. Synthesis and characterization of oxide cathode materials of the system (1-x-y) LiNiO₂ · xLi₂MnO₃ · yLiCoO₂. *Ionics* **2010**, *16*, 591–602. [[CrossRef](#)]
21. Sun, Y.; Shiosaki, Y.; Xia, Y.; Noguchi, H. The preparation and electrochemical performance of solid solutions LiCoO₂–Li₂MnO₃ as cathode materials for lithium ion batteries. *J. Power Sources* **2006**, *159*, 1353–1359. [[CrossRef](#)]
22. Jiang, J.; Eberman, K.W.; Krause, L.J.; Dahn, J.R. Structure, Electrochemical Properties, and Thermal Stability Studies of Cathode Materials. *J. Electrochem. Soc.* **2005**, *152*, A1879–A1889. [[CrossRef](#)]
23. Zhong, Q.; Bonakdarpour, A.; Zhang, M.; Gao, Y.; Dahn, J.R. Synthesis and Electrochemistry of LiNix Mn(2 – x)O₄. *J. Electrochem. Soc.* **1997**, *144*, 205–213. [[CrossRef](#)]
24. Laidler, K.J. The development of the Arrhenius equation. *J. Chem. Educ.* **1984**, *61*, 494. [[CrossRef](#)]
25. Zhang, S.; Xu, K.; Jow, T. Low-temperature performance of Li-ion cells with a LiBF₄-based electrolyte. *J. Solid State Electrochem.* **2003**, *7*, 147–151. [[CrossRef](#)]
26. Nagpure, S.C.; Dinwiddie, R.; Babu, S.; Rizzoni, G.; Bhushan, B.; Frech, T.; Power, J. Thermal diffusivity study of aged Li-ion batteries using flash method. *J. Power Sources* **2010**, *195*, 872–876. [[CrossRef](#)]
27. Nagasubramanian, G. Electrical characteristics of 18650 Li-ion cells at low temperatures. *J. Appl. Electrochem.* **2001**, *31*, 99–104. [[CrossRef](#)]
28. Aris, A.M.; Shabani, B. An Experimental Study of a Lithium Ion Cell Operation at Low Temperature Conditions. *J. Energy Procedia* **2017**, *110*, 128–135. [[CrossRef](#)]
29. Xiao, M.; Choe, S.Y. Theoretical and experimental analysis of heat generations of a pouch type LiMn₂O₄/carbon high power Li-polymer battery. *J. Power Sources* **2013**, *241*, 46–55. [[CrossRef](#)]
30. Zhang, X. Thermal analysis of a cylindrical lithium-ion battery. *J. Electrochim. Acta* **2011**, *56*, 1246–1255. [[CrossRef](#)]
31. Lu, W.; Prakash, J. In Situ Measurements of Heat Generation in a Li/Mesocarbon Microbead Half-Cell. *J. Electrochem. Soc.* **2003**, *150*, A262. [[CrossRef](#)]
32. Fengab, X.; Ouyanga, M.; Liua, X.; Lua, L.; Xiaa, Y.; Heab, X. Thermal runaway mechanism of lithium ion battery for electric vehicles. *Energy Storage Mater.* **2018**, *10*, 246–267. [[CrossRef](#)]
33. Finegan, D.P.; Scheel, M.; Robinson, J.B.; Tjaden, B.; Hunt, I.; Mason, T.J.; Millichamp, J.; Di Michiel, M.; Offer, G.J.; Hinds, G.; et al. In-operando high-speed tomography of lithium-ion batteries during thermal runaway. *Nat. Commun.* **2015**, *6*, 6924. [[CrossRef](#)]
34. Mai, S.; Wessel, J.; Dimitrova, A.; Stich, M.; Ivanov, S.; Krischok, S.; Bund, A. Nanoscale Morphological Changes at Lithium Interface, Triggered by the Electrolyte Composition and Electrochemical Cycling. *J. Chem.* **2019**, *2019*, 1–13. [[CrossRef](#)]
35. Grossi, M.; Riccò, B. Electrical impedance spectroscopy (EIS) for biological analysis and food characterization: A review. *J. Sens. Sens. Syst.* **2017**, *6*, 303–325. [[CrossRef](#)]
36. Liao, L.; Zuo, P.; Ma, Y. Effects of temperature on charge/discharge behaviors of LiFePO₄ cathode for Li-ion batteries. *J. Electrochim. Acta* **2012**, *60*, 269–273. [[CrossRef](#)]
37. Pięłowska, M.; Kurc, B.; Rymaniak, Ł. Starch as the flame retardant for electrolytes in lithium ion cells. *Materials* **2022**, *15*, 523. [[CrossRef](#)] [[PubMed](#)]
38. Magar, H.S.; Hassan, R.Y.A.; Mulchandani, A. Electrochemical Impedance Spectroscopy (EIS): Principles, Construction, and Biosensing Applications. *Sensors* **2021**, *21*, 6578. [[CrossRef](#)] [[PubMed](#)]
39. Scholz, F. Voltammetric techniques of analysis: The essentials. *ChemTexts* **2015**, *1*, 17. [[CrossRef](#)]
40. Chagnes, A. Lithium Battery Technologies: Electrolytes. In *Lithium Process Chemistry*; Chagnes, A., Swiatowska, J., Eds.; Elsevier: Chicago, IL, USA, 2015.
41. Suresh, P.; Shukla, A.; Munichandraiah, N. Temperature Dependence Studies of A.C. Impedance of Lithium-Ion Cells. *J. Appl. Electrochem.* **2002**, *32*, 267–273. [[CrossRef](#)]

42. Swiderska-Mocek, A.; Jakobczyk, P.; Rudnicka, E.; Lewandowski, A. Flammability parameters of lithium-ion battery electrolytes. *J. Mol. Liq.* **2020**, *318*, 113986. [[CrossRef](#)]
43. Pięłowska, M.; Kurc, B.; Rymaniak, L. Application of Carbonized Starches as Carbon Electrode Active Material Compared to Graphene Nanoplatelets-Based Anode in a Lithium-Ion Cell. *Waste Biomass Valorization* **2021**, *12*, 6403–6422. [[CrossRef](#)]
44. Page, J.E. Recent Developments in Polarographic Analysis. *Nature* **1944**, *154*, 199–202. [[CrossRef](#)]
45. Chauhan, C. Contemporary Voltammetric Techniques and Its Application to Pesticide Analysis: A Review. *J. Mater. Today Proc.* **2021**, *37*, 3231–3240. [[CrossRef](#)]
46. Hess, S.; Wohlfahrt-Mehrens, M.; Wachtler, M. Flammability of Li-Ion Battery Electrolytes: Flash Point and Self-Extinguishing Time Measurements. *J. Electrochem. Soc.* **2015**, *162*, A3084–A3097. [[CrossRef](#)]
47. Juszcak, L.; Witczak, M.; Zięba, T.; Fortuna, T. Rheological Behaviour of Heated Potato Starch Dispersions. *J. Int. Agrophys.* **2012**, *26*, 381–386. [[CrossRef](#)]
48. Ai, Y.; Jane, J.-L. Gelatinization and Rheological Properties of Starch. *J. Starch Stärke* **2015**, *67*, 213–224. [[CrossRef](#)]
49. Haj-Kacem, R.; Ouerfelli, N.; Herráez, J.; Guettari, M.; Hamda, H.; Dallel, M. Contribution to Modeling the Viscosity Arrhenius Type Equation for Some Solvents by Statistical Correlations Analysis. *Fluid Phase Equilib.* **2014**, *383*, 11–20. [[CrossRef](#)]
50. Duan, L.; Wang, L.; Inge, A.K.; Fischer, A.; Zou, X.; Sun, L. Insights into Ru-Based Molecular Water Oxidation Catalysts: Electronic and Noncovalent-Interaction Effects on Their Catalytic Activities. *Inorg. Chem.* **2013**, *52*, 7844–7852. [[CrossRef](#)] [[PubMed](#)]
51. Dutton, P.L.; Munro, A.; Scrutton, N.S.; Sutcliffe, M. Introduction. Quantum Catalysis in Enzymes: Beyond the Transition State Theory Paradigm. *Philos. Trans. R. Soc. B Biol. Sci.* **2006**, *361*, 1293–1294. [[CrossRef](#)]
52. Dagger, T.; Rad, B.R.; Schappacher, F.M.; Winter, M. Comparative Performance Evaluation of Flame Retardant Additives for Lithium Ion Batteries—I. Safety, Chemical and Electrochemical Stabilities. *Energy Technol.* **2018**, *6*, 2011–2022. [[CrossRef](#)]
53. Chawla, N.; Bharti, N.; Singh, S. Recent Advances in Non-Flammable Electrolytes for Safer Lithium-Ion Batteries. *Batteries* **2019**, *5*, 19. [[CrossRef](#)]
54. Nakajima, T.; Hirobayashi, Y.; Takayanagi, Y.; Ohzawa, Y. Reactions of Metallic Li or LiC₆ with Organic Solvents for Lithium Ion Battery. *J. Power Sources* **2013**, *243*, 581–584. [[CrossRef](#)]
55. Wu, M.; Xu, B.; Ouyang, C. Physics of Electron and Lithium-Ion Transport in Electrode Materials for Li-ion Batteries. *J. Chin. Phys. B* **2015**, *25*, 018206. [[CrossRef](#)]
56. Zhao, X.; Zhang, X.; Li, C.; Sun, X.; Liu, J.; Wang, K.; Ma, Y. High-Performance Lithium-Ion Capacitors Based on CoO-Graphene Composite Anode and Holey Carbon Nanolayer Cathode. *ACS Sustain. Chem. Eng.* **2019**, *7*, 11275–11283. [[CrossRef](#)]
57. Delacourt, C.; Poizot, P.; Levasseur, S.; Masquelier, C. Size Effects on Carbon-Free LiFePO₄ Powders: The Key to Superior Energy Density. *J. Electrochem. Solid-State Lett.* **2006**, *9*, A352. [[CrossRef](#)]

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