

CR2016 COIN CELL BATTERY PERFORMANCE WITH $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ CATHODES USING CONDUCTIVITY PARAMETERS, CHARGING MECHANISMS AND A LITHIUM DIFFUSION

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ABSTRACT

The mechanism for the conductivity and charging/discharging parameters of the battery has been performed to investigate the performance of the CR2016 coin cell battery, which includes the characteristics of resistance, electrical conductivity as well as the charging and discharging mechanisms of $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$, Lithium Metal Anode (Li), LiPF_6 Electrolyte, Polypropylene (PP) membrane separator, and PVDF/NMP active ingredient. A standard deviation (SD) value of 1% with a range of electrical conductivity of $2.2 \times 10^{-2} \text{ S/cm}$ - $2.4 \times 10^{-2} \text{ S/cm}$ was obtained based on the measurements of 8-coin cell battery samples. The highest material charging capacity value was obtained as 125 mAh/g in the 10th cycle and has a lithium diffusion (D_{Li}) of $2.33 \times 10^{-7} \text{ S/cm}^2$.

Keywords: Conductivity, $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$, Charging, Discharging, Lithium Diffusion.

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INTRODUCTION

A battery can produce electrical energy from chemical energy through its active material as well as electrochemical reduction and oxidation reactions.¹ The lithium-ion battery is categorized as a secondary rechargeable battery which is important for storing energy and supporting renewable energy. The lithium-ion battery has high efficiency, a long-life cycle, and high specific energy. Thus, the lithium-ion battery has been preferred as a power source for the electronics markets.² This battery is also promising for electric vehicle applications. However, there are some problematic issues such as materials availability, cost, and safety.^{3,4} Another widely used lithium battery is the lithium iron phosphate (LiFePO_4) which has a capacity of 170 mAhg⁻¹. In addition, this battery has excellent cycling stability and is environmentally benign. However, there are also drawbacks related to this battery such as slow lithium-ion diffusion and small electronic conductivity leading to poor high-rate performance.⁵ Thus, various attempts have been performed to raise the conductivity of LiFePO_4 such as through carbon coating, metal doping⁶, and Size Controlling.⁷ This study was carried out to synthesize a CR2016 coin cell battery with $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode. To prepare $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$, a solution of 0.005 wt% LiH_2PO_4 (Sigma Aldrich) was placed at ambient temperature to a mixed 0.495 wt% (Sigma Aldrich). The simultaneous Thermogravimetric-Differential Thermal Analyzer (TG-DTA) is used for thermal characterization.⁸ Samples weighing 1 mg were heated to a temperature value that ranges from the ambient temperature to 830°C with a rate of heating as 5°C per minute in atmospheric air with 100 ml per minute of flow rate. The composition of the precipitate (Fe, P) is obtained by Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS). The goniometer is then mounted on a line-shaped radiation and is positioned with a monochromator. We have recently shown that polypropylene can be used as the membrane of CR2016 coin cell battery⁹ and the aim of this work is to produce a better cathode material that is characterized by high conductivity. The commercialization of a coin cell using a LiMnO_2 cathode with a SOC (State of Charge) voltage of 3.2 V

and has a specific capacity of 90 mAh/g and a conductivity value of 10^{-9} S/cm is also anticipated. The assembly of the CR2016 coin cell battery using $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4$ doped Gadolinium (Gd) is further expected to produce a battery with better conductivity, efficiency, charging, and discharging as a parameter of battery performance. $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode of CR2016 coin cell battery were independent variables and the other component such as electrolyte $\text{LiPF}_6(\text{Aq})$, separator polypropylene (PP), and the anode lithium metal ($\text{Li}_{(\text{s})}$) were dependent variables.

EXPERIMENTAL

Material and Methods

Active materials such as $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ (LFP, 80wt%), conductive additive with a weight percentage of 5, and polyvinylidene fluoride (PVDF) of 10 weight percentage with N-methyl-2-pyrrolidone used as a cathode material binder were used in this work. In addition, battery components including electrolytes of $\text{LiPF}_6(\text{Aq})$, separator polypropylene (PP), and the anode lithium metal ($\text{Li}_{(\text{s})}$) were also utilized. The CR2016 coin cell battery was made of a positive case, spacer, spring, and negative case. This work proceeds by synthesizing the cathode, assembling the coin cell battery, and measuring the performance.

General Procedure

Active materials of $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$, PVDF, and the conductive additive were stirred for 4 hours when mixed in N-methyl-2-pyrrolidone. Graphene was used as a conductive additive. Al-foil was then used for coating the homogenous slurries which were then dried at 100°C for a duration of 10 hours. The cathode sheet was dried at 120°C for 12 hours in a vacuum after being punched into a disc. Polypropylene as a separator, Li metal as the anode, and 1 M LiPF_6 as the electrolyte were then used to assemble the CR2016 coin cells in an argon-filled glove box. The same method was used for the reference cells using 5 wt% graphite, 10 wt% PVDF, and 80 wt% LFP. The compositions and morphologies of LFP cathodes were then studied using SEM as also used in the previous work.¹⁰ X-ray diffraction with a monochromatized source of Cu K α 1 radiation ($\lambda = 0.15405$ nm) was used to identify the phase and crystalline structure of LFP cathodes. LCR meter (Hioki) was then utilized for Electrochemical Impedance Spectroscopic (EIS) measurements. EIS was preferred in this work over another widely used Raman Spectroscopy.¹¹ Charge-discharge characteristics were then tested in a voltage range of 2.5–4.2 V (0.1 C rate) on a BTS8 instrument (MTI Co.) for cell tests at room temperature. The general synthesis procedure of $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode is shown in Fig.-1.

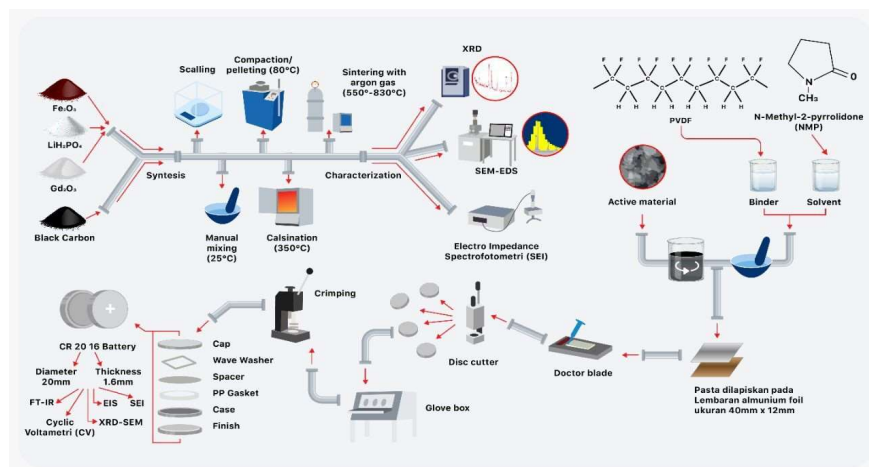


Fig.-1: General Procedure Synthesis $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ Cathode and CR2016 Coin Cell Battery

RESULTS AND DISCUSSION

The crystallographic structure of the $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode and X-ray diffraction measurements were carried out for both $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ powder cathodes in various synthesis temperatures. The XRD of the $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode is shown in Fig.-2, where there is an ordering phase for FePO_4 based on the diffraction pattern which is well indexed with (JCPDS No. 81-1173). The space group crystal is

62/*pnma* orthorhombic. From this pattern, the highest intensity and background are achieved in the LiFePO_4 phase order at a temperature of 830°C.

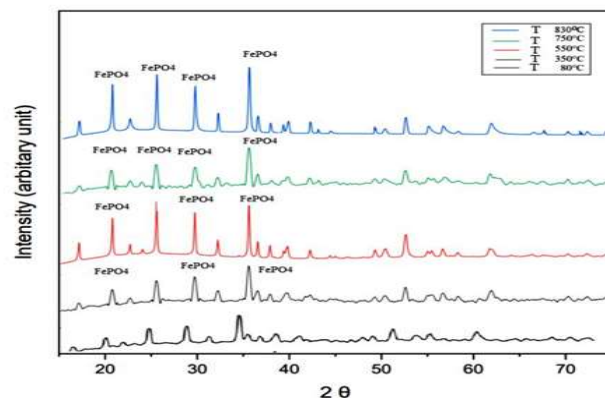


Fig.-2: X-ray Diffraction of as-synthesized $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ at Different Temperatures

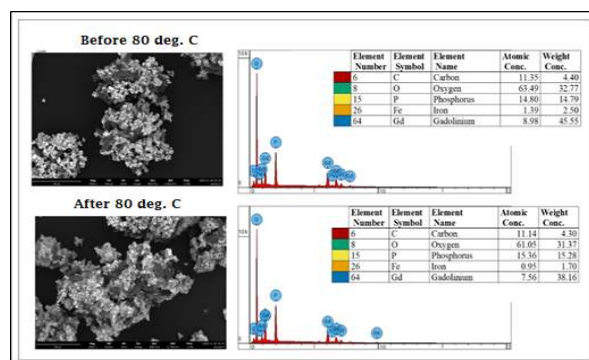


Fig.-3: SEM-EDS Images of $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ Before and After Heating at 80°C

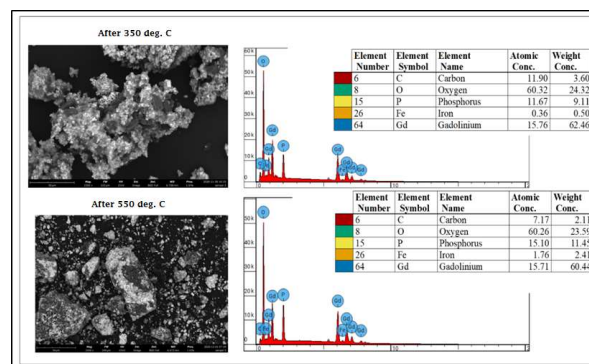


Fig.-4: SEM-EDS Images of $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ After Heating at 350°C and 550°C

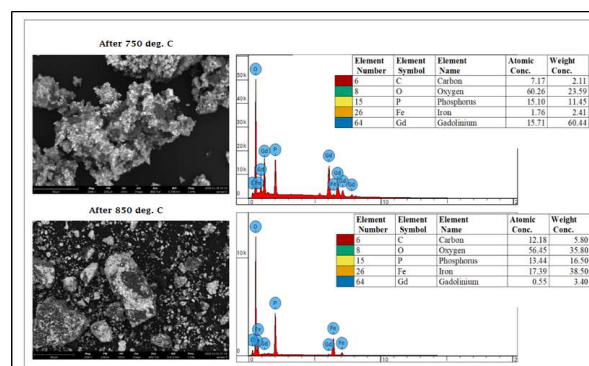


Fig.-5: SEM-EDS Images of $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ After Heating at 750°C and 830°C

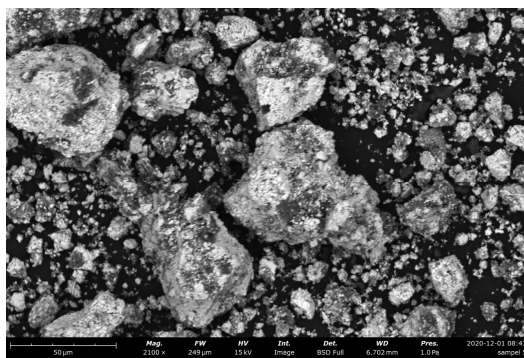


Fig-6: SEM Images of $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ After Dried and Vacuumed at 120°C After a Slurry Process

Figure-3, 4, 5 and 6 show SEM Images (magnification $\times 2100$) of several heating steps during the synthesis of $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode before and after heating at 80°C , after heating at 350°C 10 hours (filled with argon gas) (c), after heating at 750°C , after heating at 830°C 10 hours (filled with argon gas). After the formation of discs occurred, they were dried at 120°C for 12 hours in the vacuum after a slurry process. Irregular particle formation by solid-state synthesis has caused inaccuracy in comparing the morphology and particle size. Nevertheless, the particle size of both samples was approximately $1\text{--}3\ \mu\text{m}$.

The Material Conductivity

A layer of $10\text{--}30\ \mu\text{m}$ thick was assembled into a coin cell to evaluate the electrical conductivity of the $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode. Then, an LCR meter was used to measure the electrical conductivity. The results showed that $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ have good electrical conductivity as shown in Table-1.

Table-1: Conductivity of $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$

Sample	Conductivity
$\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$	$2.17 \times 10^{-4}\ \text{S/Cm}$

Prepared $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode sheets were then assembled into coin cells to investigate their electrochemical performance. The impedance spectrum of the CR2016 $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ coin cell was then measured using EIS. Figure-7 shows the Cole-Cole plot of the CR2016 $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ coin cell. It is shown that the EIS spectrum consists of a semicircle in the medium to the high-frequency range and straight slashes are located in the region of low frequency. In addition, the total resistance of the LiFePO_4 cathode can be acquired from the semicircular junction with the real axis located on the lower side of the frequency. The main reason is due to the transfer of charge between the interface of the electrode and electrolyte.

The total resistance of the CR2016 $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ coin cell is $1.39 \times 10^2\ \Omega$ which is much smaller than the $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode which is $1.15 \times 10^3\ \Omega$. This means that there is a significantly superior interface contact with the active ingredient $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$, providing greater electrical conductivity and improved charge transfer as can be seen in Table-2. Finally, the resistance of charge transfer of the insertion/extraction of Li^+ for the CR2016 $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ coin cell turned out to be greater than that for the $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode. Therefore, the $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ CR2016 coin cell battery is anticipated to produce significant prospects in the lithium-ion battery.

Table-2: The Resistance of $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ Cathode and CR2016 $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ Coin Cell Battery

No	Sample	Resistance(R_s) (Ω)
1.	CR2016 $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$	1.39×10^2
2.	$\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ cathode	1.15×10^3

The Cole-Cole plot of CR2016 $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ coin cell battery can be seen in Fig.-7. Fig-7 shows the electrochemical characteristics of the CR2016 coin cell battery expressed as ohmic resistance $R_{CT}(\Omega)$ which is also taken into consideration because the PVDF polymer chain has the electrochemically insulating

property, which can be dissolved into NMP solvent as loops and tails. An impedance analyzer was then used to measure the electrochemical responses of the sample under experimental conditions which include every step of the heating temperature. The impedance spectra of the CR2016 coin cell battery are also given by the Cole-Cole plot. The Cole-Cole plot of the CR2016 coin cell battery was made of a quarter circle with a polynomial line. The right quarter circle in the high-frequency range represents the composition of PVDF-NMP- $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}-\text{LiPF}_6$ with a lithium metal sheet (Li) as a fixed variable for the anode.

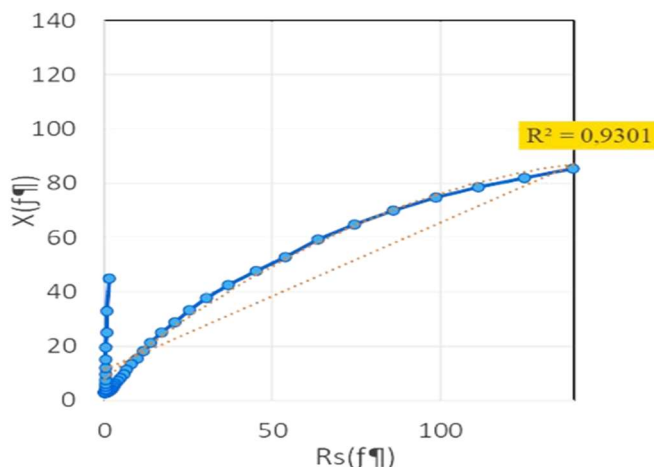


Fig.-7: The Cole-Cole Plot of CR2016 $\text{LiFe}_{0.09}\text{Gd}_{0.01}\text{PO}_4/\text{C}$ Coin Cell Battery

The Specific Capacity

The ability of batteries to store energy in milliampere hours (mAh) under charge conditions is called specific capacity. The specific capacity unit of mAh describes how much load a battery can supply for 1 hour to the lowest point. The specific capacity of the CR2016 coin cell battery can be seen in Fig.-8. The specific capacity with LiFePO_4 cathode is higher than other lithium batteries. However, the energy density is smaller because the operating voltage is lower in charge/discharging characterization. In Fig.-8, it is analyzed that the specific capacity of the battery on the 10th cycle is 125 mAh/g with the maximum voltage of the charging process reaching 3.5 V.

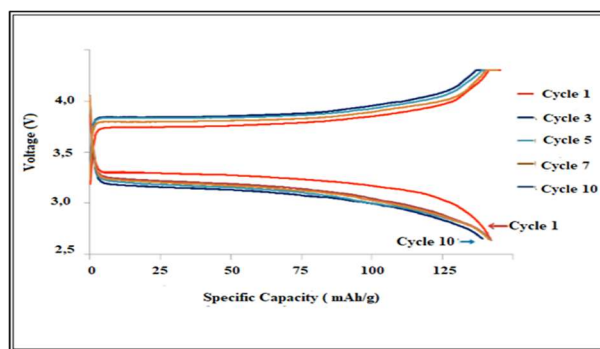


Fig.-8: The Specific Capacity of CR2016 Coin Cell Battery

The Material Polarization

In Fig.-9, it is obtained that polarization activation (for 35 seconds) occurs once every 20 seconds in the charging process with an average voltage of 3.1 V - 3.2 V.

This condition describes the polarity of the cathode which allows the movement of lithium ions (Li^+) from the cathode to the anode and vice versa. Charging and discharging profiles describe the process of polarizing very small concentrations that occurs at 4200 seconds to 4400 seconds. Furthermore, the polarization of measured concentrations is unstable. There is a polarized small-scale concentration or then a polarized high-scale concentration, and along with this gives rise to a high polarization ohm. U_0 is 3.1 V, U_2 is average at 2.5 V, and U_1 has a value almost the same as U_3 which is 3V. This indicates that the optimum State of Charge is at 2.38 V – 2.4 V or about 30%. Since the internal polarization voltage of lithium-ion batteries is relatively small, the control strategy that leads to the negative pulse charging strategy in the charging process

is able to promote the charge rate of lithium-ion batteries, seen from -30% until then it can be increased up to every 10 scales until it reaches a maximum of 30%.

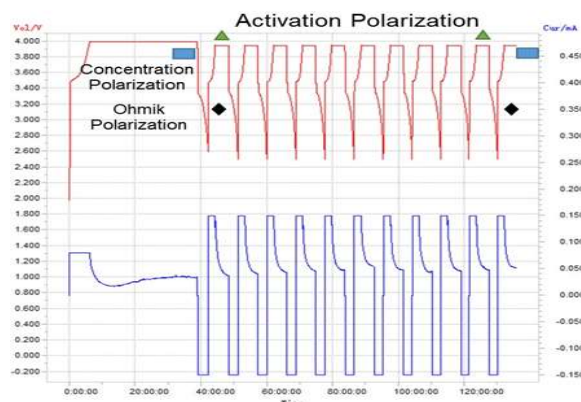


Fig.-9: Charging and Discharging of CR2016 Coin Cell Battery

Lithium Diffusion (D_{Li})

Lithium diffusion (D_{Li}) describes the movement of Li^+ from the cathode towards the anode through a separator and submerged in the electrolyte. The anode used is in the form of a metal $Li(s)$ separator in the form of polypropylene (PP) and the electrolyte is a $LiPF_6(Aq)$ solution in ethyl carbonate/diethyl carbonate EC/DEC solvents in a ratio of 1:1 (v/v). Lithium diffusion (D_{Li}) of $LiFe_{0.09}Gd_{0.01}PO_4/C$ can be seen in Fig.-10. Lithium diffusion (D_{Li}) of $LiFe_{0.09}Gd_{0.01}PO_4/C$ can be seen in Table-3.

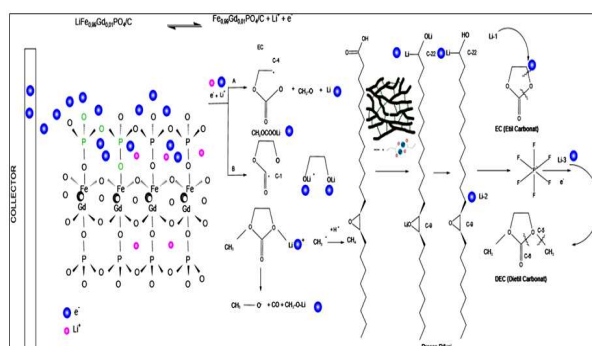


Fig.-10: Lithium Diffusion (D_{Li}) Mechanism of $LiFe_{0.09}Gd_{0.01}PO_4/C$

Table-3: Lithium Diffusion (D_{Li}) of $LiFe_{0.09}Gd_{0.01}PO_4/C$

Coin Cell	D_{Li} (S/cm^2)
CR2016 with a thickness of 0.2 μm	2.33×10^{-7}

Based on the work of (Prosini, 2002), it was obtained that the value of D_{Li} in $Li_{1-x}FePO_4$ at the smallest to largest x ranges from $1.29 \times 10^{-14} S/cm^2$ - $9.13 \times 10^{-15} S/cm^2$. The value obtained at the $LiFe_{0.09}Gd_{0.01}PO_4/C$ cathode averages $1.30 \times 10^{-7} S/cm^2$. A good diffusion coefficient value describes the possibility that rapid diffusion of Li^+ occurs at $LiFe_{0.09}Gd_{0.01}PO_4/C$.¹²

CONCLUSION

The CR2016 $LiFe_{0.09}Gd_{0.01}PO_4/C$ coin cell has a good new start of electrochemical performances with an increased electrical conductivity of the cathodes. Specifically, the specific capacity is obtained as 125 mAh/g after the 10th cycle of the CR2016 $LiFe_{0.09}Gd_{0.01}PO_4/C$ coin cell battery. It could be concluded that CR2016 $LiFe_{0.09}Gd_{0.01}PO_4/C$ has improved the performance of the $LiFePO_4$ lithium-ion battery but can be more developed to increase the electrochemical performances in the future.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHORS CONTRIBUTION

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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