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MINI-REVIEW: THE INFLUENCE OF COATING AND DOPING ON THE CRYSTAL VOLUME AND DISCHARGE CAPACITY OF LITHIUM IRON PHOSPHATE-BASED MATERIALS AS BATTERY CATHODE

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ABSTRAK

Baterai ion litium adalah jenis baterai isi ulang yang memiliki kapasitas tinggi, potensi elektrokimia yang baik, dan daya tahan yang kuat. Perkembangan $LiFePO_4$ sebagai material katoda baterai ion litium semakin meningkat dengan adanya beberapa teknik tambahan dalam proses sintesis untuk meningkatkan performa seperti teknik pelapisan dan penyisipan atom. Hal tersebut mempengaruhi volume kristal, serta sifat elektrokimia material berbasis $LiFePO_4$. Metode pelapisan yang menunjukkan peningkatan nilai kapasitansi material berbasis $LiFePO_4$. Sedangkan pada metode penyisipan atom, beberapa penelitian menggunakan atom Ce, Ru, Co, Na, Si, Mn, Zn dan In untuk disisipkan di atom Fe, Li, atau P pada material berbasis $LiFePO_4$. Hasil yang diperoleh dari beberapa penelitian tentang sintesis material katoda $LiFePO_4$ menunjukkan adanya peningkatan kapasitas discharging dan peningkatan volume kristal olivine, sehingga teknik pelapisan dan penyisipan ini dapat digunakan untuk peningkatan performa elektrokimia.

Kata kunci: $LiFePO_4$, Pelapisan, Penyisipan, Volume Kristal, Kapasitansi

ABSTRACT

Lithium-ion batteries are a type of rechargeable battery that has high capacity, good electrochemical potential, and strong durability. The development of $LiFePO_4$ as a cathode material for lithium-ion batteries has been increasing with the addition of several techniques in the synthesis process to enhance performance, such as coating and atom insertion techniques. These techniques affect the crystal volume and the electrochemical properties of $LiFePO_4$-based materials. Coating methods have shown improvements in the capacitance values of $LiFePO_4$-based materials. Meanwhile, in atom insertion methods, some studies have used Ce, Ru, Co, Na, Si, Mn, Zn, and In atoms to be inserted into Fe, Li, or P atoms in $LiFePO_4$-based materials. Results from several studies on the synthesis of $LiFePO_4$ cathode materials have shown an increase in discharge capacity and an increase in the volume of olivine crystals, indicating that coating and insertion techniques can be used to improve electrochemical performance.

Keywords: $LiFePO_4$, Doping, Coating, Crystal Volume, Capacity

I. INTRODUCTION

Lithium-ion battery is an electronic device that is being developed a lot because of its wide use. The lithium-ion battery is a type of secondary battery or rechargeable battery that has a high capacitance, high electrochemical potential, and good durability (1). Based on several studies, $LiFePO_4$ material is one lithium-ion battery cathode that has been widely developed because of its advantages compared to other cathode materials. $LiFePO_4$ has several advantages including high capacitance, thermal stability, long life cycle, safety because it can be synthesized using environmentally friendly materials, and low production costs (2). One of the lithium-ion battery cathodes that have been synthesized in previous studies is from $LiFePO_4$-based material (3, 4). The electrode (anode and cathode), separator, and electrolyte are the main components of a lithium-ion battery (5). The electrodes are used to release and accept the electrons. The separator functions as a barrier between the anode and cathode that ions can pass through, while the electrolyte is a liquid that functions for reduction-oxidation processes and as a medium for ion transport or transfer. The process that occurs when discharging or discharging, namely the anode releases electrons towards the negative terminal and flows up to the cathode. One of the components of the lithium-ion battery is the cathode (6).

The process of converting chemical to electrical energy is called an electrochemical process (7). This electrochemical process that occurs at the battery electrodes is called the charge-discharge process. During the discharge process, Lithium (Li^+) ions are transferred, depicted by a small red circle, from the cathode to the anode and back during the charging process. Pure $LiFePO_4$ has Fe^{2+} ions in its valence state. The release of Li^+ ions causes defects so that $LiFePO_4$ tends to have Fe^{3+} ions. In addition, the change from Fe^{2+} to Fe^{3+} can be caused by the oxidation of the Fe atom. Li^+ ions are released from the anode and fill the cathode during the discharge process. Meanwhile, Li^+ ions move from the cathode to the anode in the charging process. The charge/discharge mechanism can be explained by the electrochemical reactions that occur during charging are shown in Equation 1, while during discharge they are shown in Equation 2.

$$LiFePO_4 - {}_xLi^+ - {}_xe^- \rightarrow {}_xFePO_4 + {}_{(1-x)}LiFePO_4 \qquad \text{... (1)}$$
$$FePO_4 + {}_xLi^+ + {}_xe^- \rightarrow {}_xLiFePO_4 + {}_{(1-x)}FePO_4 \qquad \text{... (2)}$$

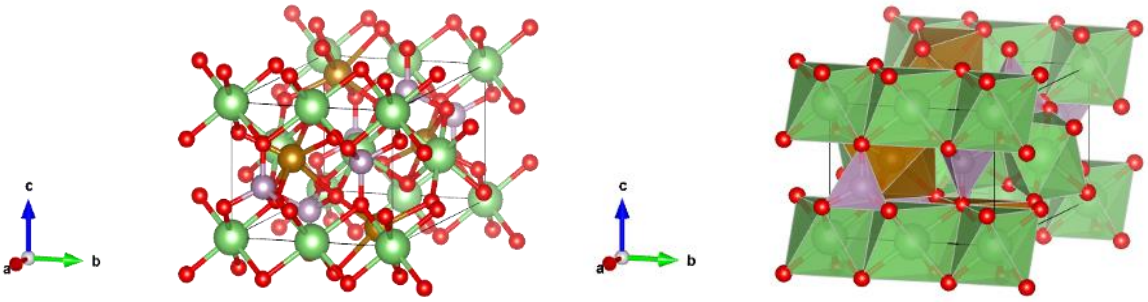
$LiFePO_4$ has great potential as cathode material for lithium-ion batteries because of its low toxicity, high charging-discharging capacity of 170 $mAh.g^{-1}$, excellent safety profile, and favorable economic advantages. Meanwhile, lithium-ion batteries that are composed of pure $LiFePO_4$ cathode material have several disadvantages, including short charge-discharge cycles, short battery life, and long charging processes but fast discharging processes that make battery performance less than optimal. However, the lack of performance of the battery cathode is due to the low conductivity and the low ion-diffusion rate, thus inhibiting its future development. In addition, some previous studies have shown that pure $LiFePO_4$ cathode materials also have lower capacitance compared to LFP cathodes that are treated with atomic doping and carbon coating (8).

To overcome these weaknesses, surface modification by coatings is often utilized. This aims to avoid unwanted interactions between electrodes and electrolytes. This method can improve the thermal and structural stability as well as the chemical and mechanical properties of cathode materials (9). The three-dimensional carbon coating on LiFePO4 enhances its high capacity, superior electrical conductivity, and minimal volumetric expansion, facilitating more efficient electron transport pathways (10). Besides coatings, doping can be applied to modified lithium oxides. Doping is the addition of a few heteroatoms that are incorporated into the host crystal structure without the appearance of additional phases. Since the structure of lithiated oxides and their electrochemical properties can vary greatly, this approach is often used to control the behavior of active materials (9).

The need for battery technology is a major requirement nowadays. The use of electronic divisions is increasing among the public, so research on battery cathode materials needs to be continuously developed. The development of this research is shown by innovations in material synthesis techniques, including coating techniques and doping techniques. This article will further discuss research that develops new techniques for improving the performance of battery cathodes, especially in lithium-ion batteries. Herein, the purpose of this review is to show material development methods with atomic doping and carbon coating techniques towards improving battery cathode performance, such as the enhancement of discharge capacitance, especially in lithium-ion batteries. This study also summarizes atoms for doping technique and their effect on olivine crystal structure. Furthermore, it also discusses materials that can be used as coatings.

II. CRYSTAL ARRANGEMENT OF $LiFePO_4$

$LiFePO_4$ exhibits the structure of FeO_6 octahedra and PO_4 tetrahedra. These tetrahedra share oxygen atoms with adjacent PO_4 tetrahedra and FeO_6 octahedra. Lithium ions are positioned between the FeO_6 octahedra and PO_4 tetrahedra. The oxygen atoms in $LiFePO_4$ adopt a configuration where each is coordinated by one Fe and one P atom. In some lithium-based oxide cathode materials, structural degradation can occur due to the migration of metal ions from octahedral to tetrahedral sites (10). $LiFePO_4$ exhibits a characteristic olivine-type crystalline structure with a lattice arrangement categorized under the P lattice type. The space group's name is Pnma. Lattice parameters of $LiFePO_4$ are a, b, c = 10.3297, 6.0115, 4.7017 Å and $\alpha = \beta = \gamma = 90°$ (11). The structure of $LiFePO_4$ is shown in Figure 1 illustrated using *Vesta software*.



(a) (b)

Figure 1. The olivine structure of $LiFePO_4$ with different views (a) ball and stick view showing red for oxygen atom, green for lithium atom, brown for ferrous atom, and purple for phosphate atom; (b) polyhedral view showing the FeO_6 octahedra (green), PO_4 tetrahedra (purple), and one-dimensional tunnels in which the lithium ions reside.

Olivine-structure of $LiFePO_4$ is considered a promising cathode material for lithium-ion batteries (12, 13). Olivine structure has a hexagonally close-packed oxygen array, in which the octahedra share both edges and faces. $LiFePO_4$ initially includes one Li^+ ion per formula unit that can be extracted and transferred to the anode in the first charge process, compensating for the oxidation of iron (Fe^{2+} to Fe^{3+}) (13). The transfer of lithium ions occurring at the interface between the electrode and electrolyte, alongside the lithium transportation within the active materials and porous electrode space, constitutes a pivotal phenomenon during the charging-discharging cycles of batteries. The efficiency of these processes significantly influences the overall battery performance, as highlighted by Qianru Shi (14). The limited electrical and ionic conductivity exhibited by LiFePO4 contributes to its diminished rate capacity and utilization. Addressing these limitations has emerged as a critical focus of research, as emphasized by Satyavani (2).

III. SYNTHESIS METHOD OF $LiFePO_4$

There are several methods in the synthesis of LiFePO4-based cathode materials such as solvothermal, hydrothermal, sol-gel, solid state, citrate process, and dissolution method. $LiFePO_4$ was synthesized using solvothermal in several studies (10, 15). The solvothermal method used a solvent for the synthesized process under elevated temperature (100-1000°C) and pressure (1-10.000 atm) (16). Solid state method is also used for $LiFePO_4$ synthesized material (17, 18 19, 20). The solid-state method is the most common method for preparing powders and is generally used for the mass production of unique and advanced structures. This method is simple and easy to industrialize (2). The hydrothermal method was also used in several studies to synthesize $LiFePO_4$ materials (3, 21). The hydrothermal process involves a heterogeneous chemical reaction occurring within an aqueous medium subjected to elevated pressure and temperature conditions. This method facilitates the dissolution and subsequent recrystallization of substances that exhibit limited solubility under standard environmental circumstances (Shaikh et al., 2020). On the other hand, the sol-gel technique represents an effective approach for attaining targeted particle dimensions with precise stoichiometry, while requiring a reduced calcination temperature and yielding high product quantities. In the specific case of LiFePO4, carbon coating was applied to integrate the organic additive during an intermediate grinding phase after initial decomposition at 500°C. This improved the rate-ability of the sol-gel material (11). Other synthesized methods for $LiFePO_4$ material are the citrate process Method (22) and the dissolution method (23).

The development of $LiFePO_4$ material for lithium-ion battery electrodes makes researchers innovate to improve this performance. There are several kinds of techniques used to make $LiFePO_4$ material that are increasingly useful. This article presents two techniques that have been widely used in several studies, coating and atomic doping method in $LiFePO_4$-based material.

IV. COATING METHOD OF $LiFePO_4$

The application of coating techniques has emerged as a pivotal strategy in enhancing the efficiency of materials. Coating, as a method of coverage applied to object surfaces, serves to enhance various surface properties of the substrate, encompassing aspects such as visual aesthetics, adhesion, corrosion resistance, and wear resistance, among others (24). Various coating methods cater to diverse application needs, all unified by the overarching objective of safeguarding components or structures from potential mechanical or chemical harm (25).

The advantages of carbon coating were highlighted, focusing on its application to newly developed photocatalyst particles and electrode materials for lithium-ion rechargeable batteries. Carbon materials have found widespread application owing to their favorable attributes, including elevated electrical and thermal conductivity, as well as robust thermal and chemical stability (26). A widely used technique to increase the conductivity of $LiFePO_4$ is carbon coating electrons (14). The electrochemical efficiency of $LiFePO_4$-coated carbon electrodes relies on the choice of carbon precursor, which encompasses organic, inorganic, polymer, and biomass sources. (27).

Elevated levels of carbon are anticipated to enhance the diffusion rate of Li+ ions across carbon layers. The transfer of lithium ions at the electrode-electrolyte interface, alongside their movement within active materials and the porous electrode structure, constitutes a pivotal aspect of battery charge-discharge cycles. The kinetics of these processes significantly enhance the battery's overall performance. Consequently, battery electrodes must exhibit robust lithium ion and electron conductivity to facilitate the efficient transport of lithium ions and electrons. (14). The application of a carbon coating additionally diminishes the particle size of $LiFePO_4$ by impeding particle expansion throughout the sintering procedure (28). The procedure involves applying carbon coatings using different carbon precursors, followed by high-temperature thermal treatment. This approach is characterized by its simplicity, feasibility, and suitability for large-scale industrial applications. The coating process serves to decrease the volumetric energy density of battery materials and constrain the diffusion of lithium ions.

The process of carbon coating on $LiFePO_4$ material used as electrode material has been carried out by many researchers using various thermal treatments in the synthesis process. Therefore, this article presents a comparison of the use of carbon sources, carbon coating synthesis methods, and the best capacitance values obtained from several studies. The comparison of capacitance values of $LiFePO_4$ electrodes treated with carbon coating is shown in Table 1.

Table 1. Comparison of synthesis method and best capacitance from each carbon source.

Carbon Sources	**Synthesis Method**	**Best Capacitance ($mAhg^{-1}$)**	**Ref.**
Glucose	Pyrolysis, annealed at 700°C for 5 hours under a N_2 atmosphere.	162	(3)

Three-dimensional carbon from *Cetyltrimethyl Ammonium Bromide* (CTAB)	Solvothermal, stirring for 8 h and annealed at 500^{o}C or 800^{o}C for 3 hours in N_2.	159.8	(10)
Polypropylene	Solvothermal and carbonization at 650^{o}C for 3 hours in Argon atmosphere	80.9	(15)
Glucose	Solid state reaction, dry mixing, ball milling and calcined at 700^{o}C for 8 hours under N_2 atmosphere.	160.1	(17)
Glycine & MWCNT	Solid state reaction, sintered at 750^{o}C for 6 hours in flowing Ar atmosphere, ball milling.	130	(18)
Tapioca and acetic acid (CH_3COOH)	Heated to 700°C for 20 minutes in a nitrogen atmosphere.	35.58	(19)
Glucose ($C_6H_{12}O_6$) 11wt%	The carbonation process is conducted within a tube furnace at a temperature of 450°C for a duration of 2 hours under a Nitrogen atmosphere.	78.745	(20)
Carbon Nano Tube (CNT)	Hydrothermal Process, annealed in the tubular furnace at 700^{o}C for 6 hours under Argon atmosphere	106.84	(29)

Based on Table 1, it is obtained that the carbon coating synthesis method for $LiFePO_4$ material uses a carbonization temperature range between 450^{o}C and 700^{o}C. In addition, several studies use natural materials as basic carbon materials, namely Glucose (20) and Tapioca (19). Besides carbon coatings, there were some other innovations with non-carbon coating in $LiFePO_4$ cathode materials. During the process of carbon coating, the augmentation in carbon content is observed to diminish the tap density of LFP particles. Conversely, the metal coating is shown to maintain the electronic density of LFP particles while circumventing any reduction in tap density. Moreover, metal coating facilitates the formation of electron channels within the external layer of the cathode material, thereby enhancing the speed of electron transport (21). Common materials for surface coating that do not contain carbon include metals, metal oxides, solid electrolytes, and ion-conducting materials. Gallium can be utilized to enhance the electrochemical performance and electron conductivity of $LiFePO_4$ (LFP) without compromising its original olivine structure (30). Furthermore, Gallium coating demonstrated that by modification of $LiFePO_4$ cathode materials with a combined gallium and carbon coating, the cycling performance and charge-discharge capacity are significantly improved compared to pristine LFP@C (21).

V. ATOMIC DOPING METHOD OF $LiFePO_4$

Doping is the process of adding very trace amounts of particular foreign atoms, called dopants, to the crystal lattice to change the electrical characteristics (31). In addition, atomic doping also aims to increase the cell volume in the crystal structure without changing the crystal phase. Increasing the cell volume in the crystal structure is expected to improve electrochemical performance, especially in battery cathode materials. Atomic dopants that are commonly used are atoms that have adjacent atomic radii, where the atomic dopant has a larger radius than the original atom. One of the studies that carried out the atomic doping technique is the use of Silicon (Si) atomic dopants against Phosphate (P) atoms in the $LiFePO_4$ structure so that the structure becomes $LiFeSi_xP_{1-x}O_4$ (19, 20).

To review the atomic doping process, it is necessary to characterize the material. One of the characterization methods that can be used to ensure the atomic doping process occurs is XRD (X-ray Diffraction). XRD is a material characterization technique that is widely used to identify the structure and phase of a material. Several studies have successfully identified the material structure, especially in $LiFePO_4$ materials that are given atomic doping techniques or carbon coating techniques (17, 33). This article presents several studies that have successfully identified atomic doping events through XRD for material structure and Discharge Capacity for electrochemical performance which is shown in Table 2.

Table 2. Comparison of various atomic doping in $LiFePO_4$ materials in volume crystal and discharge capacity performance.

Sample	**Dopant Atom**	**Doping Site**	**Crystal Volume (Å^3)**	**Discharging Capacity (mAhg^{-1})**	**Ref.**
$LiFePO_4/C$	-	-	285.06	N/A	(11)
$LiFe_{0.99}Ru_{0.01}PO_4/C$	Ru	Fe	281.64	162.6 - 110.6	
$LiFePO_4$	-	-	286.87	64.4 - 49.3	(15)
$Li_{0.99}Na_{0.01}FePO_4$	Na^+	Li	287.79	80.9 - 70.1	
$LiFePO_4/C$	-	-	290.61	147.6	(17)
$LiFe_{0.95}Ce_{0.05}PO_4/C$	Ce^{3+}	Fe	290.88	160.1 - 136.7	
$LiFePO_4/C$	-	-	N/A	130 – 20	(18)
Co-doped $LiFePO_4/C$	Co	N/A	N/A	110 – 70	
$LiFePO_4/C$	-	-	291.04	23.22	(19)
$LiFeSi_{0.15}P_{0.85}O_4/C$	Si	P	291.14	35.58	
$LiFePO_4/C$	-	-	289.35	51.715	(20)
$LiFeSi_{0.03}P_{0.97}O_4/C$	Si	P	290.78	78.745	
$LiFePO_4$	-	-	N/A	N/A	(23)
$LiFe_{0.98}Cu_{0.02}PO_4$	Cu	Fe	281.11	13.73	
$LiFePO_4@C$	-	-	291.18	140	(33)
$LiFe_{0.97}In_{0.03}PO_4$	In	Fe	291.55	150	
$LiFePO_4$	-	-	287.04	88	(34)
$LiZn_{0.01}P_{0.99}O_4$	Zn	P	293.54	133	
$LiFePO_4@C$	-	-	290.65	138.7	

$LiFe_{0.98}Mn_{0.02}PO_4$@C	Mn	Fe	290.86	150.7	(35)

The X-ray diffraction (XRD) analysis revealed a notable augmentation in the crystalline volume of $LiFePO_4$-based materials across all doped variants while retaining the olivine structure indexed in orthorhombic P n m b. The introduction of a minor quantity of Cesium dopant atom did not disrupt the lattice configuration of $LiFePO_4$; rather, it led to an expansion in crystal volume. This phenomenon was accompanied by an increase in the lattice parameters of all crystal cells, attributed to the incorporation of Ce^{3+} ions instead of Fe^{2+}, possibly due to the larger ionic radius of Ce^{3+} (r = 0.114 nm) compared to Fe^{2+} (r = 0.074 nm) occupying the Fe sites (17). Conversely, XRD analysis of Ruthenium-doped samples exhibited a reduction in the volume of $LiFePO_4$-based material crystals, accompanied by a decrease in lattice parameters. This reduction in lattice parameter shortens the path of Li^+ movement and reduces diffusion distances in Ru-doped $LiFePO_4$ (11). Moreover, changing copper atoms or doping into the Iron sites may enhance the kinetics of electrochemical processes due to the increased electrical conductivity imparted by Copper within the $LiFePO_4$-based material (23). Another study on Na^+ atomic doping indicates that the lattice structure of $LiFePO_4$ was unaffected by a small amount of Na ion doping. Since the Na^+ radius of 0.97 Å is larger than the Li+ radius (0.68 Å), Na-doped $LiFePO^4$ had a larger lattice size than pure LiFePO4, which was beneficial for the Li+ intercalation/deintercalation process (15).

Based on the crystal volume data presented in Table 2, it is evident that most $LiFePO_4$ samples doped with Si exhibit an increase in crystal volume. This increase is attributed to the expansion of the crystal lattice parameters, which occurs as the doping concentration rises. The introduction of Si ions, which possess larger crystal dimensions compared to P ions, results in the observed lattice parameter enlargement (19). Consequently, the enhancement of lattice parameters, particularly the 'x' parameter, is primarily due to the larger atomic diameter of Si relative to P atoms. This observation confirms the successful incorporation of Si into the parent phase without altering the overall crystal structure (20). Doping Ruthenium (Ru) into iron (Fe) sites demonstrates advantageous effects in enhancing electron and Li^+ transmission capabilities through the reduction of lattice parameters and band gap, alongside the elevation of Fermi energy. Ru doping significantly improves both the lithium diffusion coefficient and electrical conductivity, leading to a marked enhancement in electrochemical performance. Notably, a minimal level of Ru doping does not alter the ordered olivine structure of $LiFePO_4$ (11).

VI. ELECTROCHEMICAL PERFORMANCE

The electrochemical performance of graphene-based materials depends on the components used in their construction, particularly on their surface area, redox couple, electroconductivity, and long-term stability. The electrochemical process that takes place on lithium-ion battery electrodes consists of charging and discharging processes. The charging-discharging processes occur due to electrochemical reactions at the respective electrodes, which are accompanied by a reversible (de) intercalation of Li^+ ions into the host electrode structures. This reversibility is important to allow the battery to recharge. These reactions must be reversible to allow a high cycle life of the battery (36). Discharging capacity is the amount of charge stored by the electrode and the maximum dependable operating capability of a charge storage resource to discharge energy. A comparison of discharging capacity values is shown in **Table 2**. Based on several studies using atomic doping, show an increase in the overall discharging capacity value, indicating that atomic doping techniques can improve the electrochemical performance of $LiFePO_4$ materials.

Furthermore, to explore the impact of doping atoms in $LiFePO_4$-based materials, the Electrochemical Impedance Spectroscopy (EIS) reveals that Ru doping results in the value of Li^+ diffusion coefficient is 1.11×10^{-11} cm^2s^{-1} and has a low charge transfer resistance (R_{CT}) of 58.40 Ω. These EIS data show that doping $LiFePO_4$ with Ru can increase Li^+ ion transfer. Additionally, the application of a carbon coating synergically affects the performance of $LiFePO_4$ (11). EIS tests demonstrate that a three-dimensional carbon coating on $LiFePO_4$ enhances the lithium-ion diffusion rate, leading to an increased specific capacity of $LiFePO_4$ (21, 37).

IV. CONCLUSION

$LiFePO_4$, a widely developed lithium-ion battery cathode material, exhibits an olivine crystal structure and oxygen atoms shared between neighboring PO_4 tetrahedra and FeO_6 octahedra. Several synthesis methods, including solvothermal, hydrothermal, sol-gel, solid-state, citrate process, and dissolution methods, have been employed to produce $LiFePO_4$-based cathode materials. Among these, the solvothermal method is frequently utilized. To enhance electrode performance, atomic doping, and coating techniques are commonly applied. Notably, three-dimensional carbon coating has been shown to improve lithium-ion diffusion rates, thereby enhancing the specific capacity of $LiFePO_4$. Continuous innovation in the fabrication and modification of $LiFePO_4$, particularly through various doping atoms and carbon sources, holds promise for significant improvements in electrode performance.

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