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Research on the tri-block copolymer-directed self-assembly synthesis of bicontinuous structures for electrical energy storage

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Abstract. The burgeoning demand for more efficient energy storage systems necessitates advancements in electrode material technologies. Bicontinuous structures, synthesized using tri-block copolymers, present a promising avenue due to their unique properties that can enhance battery performance. This study aims to explore the potential of tri-block copolymer-directed self-assembly in synthesizing bicontinuous structures and to assess their application as innovative electrode materials in electrical energy storage systems. It was found that the synthesized bicontinuous structures demonstrate superior ionic pathways, resulting in enhanced ion transport and improved electrochemical performance compared to traditional electrode materials. The copolymers contribute to the formation of a highly ordered mesoporous architecture, leading to increased surface area and more active sites for electrochemical reactions. Furthermore, these structures exhibit significant stability during cycling, attributed to their ability to accommodate volume expansions and distribute mechanical stress effectively. Future research should focus on the extension of the synthesis process and the further optimization of the electrochemical properties in order to make the transition from laboratory studies to practical applications.

Keywords: Tri-Block Copolymer, Self-Assembly, Bicontinuous Structure, 3D Battery.

1. Introduction

In recent years, as the global energy landscape transitions to renewable energy sources, the demand for advanced energy storage systems with high energy density, stability and sustainability has increased dramatically. This shift has underscored the need for innovative materials and technologies capable of meeting the evolving demands of energy storage. Electrode materials are pivotal in determining the efficiency, capacity, and life cycle of energy storage devices. Innovations in material synthesis and structure are critical for achieving improvements in battery performance, particularly in terms of energy density and charge/discharge efficiency [1][2]. Despite the promising capabilities of tri-block copolymers in forming structured nanomaterials, their application in synthesizing bicontinuous structures for energy storage remains inadequately explored. There is a substantial opportunity to harness their self-assembly properties to improve ion transport and mechanical stability in batteries. This paper aims to synthesize bicontinuous structures using tri-block copolymer directed self-assembly and to investigate their potential as innovative electrode materials for electrical energy storage. Therefore, it is hypothesized that these structures will provide superior ion transport pathways and increase surface area, thereby improving battery performance. The directed self-assembly of triblock copolymers offers a transformative approach to the field of electrical energy storage, as it allows for the synthesis of bicontinuous structures.

2. Tri-Block Copolymers in Electrical Energy Storage

2.1. Overview of Alkali Metal Ion Batteries

The rapid development of various modern applications, from portable electronics to automobiles, has increased the demand for rechargeable batteries. Alkali metal ion batteries are popular due to their simple processing procedures and wide range of applications [3]. Traditional alkali metal batteries rely on ion exchange between an anode made of graphite or metal oxide and a compound cathode to facilitate charging and discharging. This means that the transmission rate of ions between the electrodes affects the battery's power density [4][5]. In alkali metal batteries, the characteristic time (τeq) for the diffusion of ions through an electrode material is determined by the square of the characteristic diffusion length (l) and diffusion coefficient (D) according to Eq. (1) [6]. To effectively reduce the diffusion time, one can choose to increase the diffusion coefficient (select an ion conductor with better performance) or reduce the characteristic diffusion length (such as constructing nanoelectrodes). It is evident that the latter is a more efficient method that avoids directly changing the electrochemical properties of the battery [7].

$$\tau_{eq} = \frac{l^2}{D} \tag{1}$$

2.2. Advantages of Employing Tri-Block Copolymers

Electrodes with bicontinuous structures constructed from tri-block copolymers offer significant advantages for improving battery performance. These structures have shorter ion diffusion paths, which accelerate ion transport during charge and discharge cycles and enhance the battery's rate capability [8]. The interconnected porous network characteristic of these materials enables superior ion transport by offering continuous channels that reduce resistance and enhance ionic conductivity [9]. Furthermore, the high surface area associated with mesoporous structures increases the number of active sites available for electrochemical reactions, thereby maximizing electrode material utilization and achieving higher capacities [10]. The structural stability of bicontinuous materials is particularly advantageous for accommodating volume expansion and distributing mechanical stress during cycling. This flexibility in the porous framework helps maintain the integrity of the electrode, extending the battery's operational life [11]. In addition, the enhanced permeability of these structures allows for better electrolyte infiltration, ensuring thorough wetting of the electrode and reducing inefficiencies during ion exchange [12]. Design flexibility is another important benefit of tri-block copolymers. The ability to modify pore sizes and volumes enables the precise optimization of electrode architecture for specific battery chemistries and applications. Therefore, this approach maintains and enhances the electrochemical properties of the battery without altering its fundamental properties, resulting in a more efficient and durable energy storage solution.

3. Self-Assembly of Block Copolymers

3.1. Self-Assembly Fundamentals and Influencing Factors

The self-assembly of block copolymers (BCPs), such as diblock copolymers, is distinct in both bulk and solution due to the inherent immiscibility of the constituent polymer blocks. In bulk, these copolymers undergo microphase separation, leading to diverse morphologies such as spheres (S), cylinders (C), bicontinuous gyroid structures (G), and lamellae (L) [13]. The selection of morphology is influenced by three critical parameters: 1) *Flory–Huggins* Interaction Parameter (χAB): This parameter measures the degree of incompatibility between the different blocks, affecting the extent of phase separation. 2) *Total*

Degree of Polymerization (*N* = *NA* + *NB*): This indicates the total polymerization degree of both blocks, affecting the stability and structure of the resulting phases. 3) *Volume Fractions* (*fA* and *fB*, where *fA* + *fB* = *1*): These fractions determine the spatial distribution and structural dominance of each block within the assembled morphology.

3.2. Self-Assembly in Electrical Energy Storage

The amphiphilic nature of BCP is utilized to synthesize mesoporous materials by template-based strategies in aqueous solution. Hydrophobic interactions between the hydrophobic blocks lead to aggregation of BCP chains to form structures stabilized by hydrophilic coronae, reducing the energy loss of the hydrophobic segments in contact with water. These aggregates result in various structures such as spherical micelles, cylindrical micelles, bicontinuous structures, lamellae, vesicles, and their inverse formations, with the final morphology determined by the packing parameter p (Eq. 2)

$$\boldsymbol{p = \frac{v}{a_0 l_c}} \tag{2}$$

where v is the volume of the hydrophobic segment, l_c denotes its length, and a_0 means the contact area of the hydrophilic block. This parameter predicts the shape and structure of micelles based on the physical dimensions and interaction dynamics of the hydrophobic and hydrophilic blocks [14].

The utilization of ABC triblock terpolymers instead of AB diblock copolymers markedly expands the scope of accessible ordered nanostructures, thereby enabling the formation of a multitude network morphologies and promoting the development of three-component nanocomposites. ABC triblock polymers are highly versatile and can be tuned to create various intricate network morphologies. Such diversity is not observed in block copolymer co-assemblies with nanoparticles, which highlights a significant advantage of pure ABC systems [15]. In addition, the network phases formed by triblock terpolymers are trifunctional, which can be expressed over a wider compositional range (4 to 14 Vol%), whereas the diblock copolymers' bis-gyroscopic structures have a more limited compositional range (2 to 6 Vol%) [16]. Extending the demonstration of these network phases in ABC terpolymer-directed composites to match or closely align with the composition range of the parent polymer could greatly enhance scalability and manufacturing feasibility, addressing the limitations posed by the narrow phase windows of diblock copolymers [17]. For instance, *PI-b-PS-b-PEO* copolymers exhibit varying hydrophilicity among the blocks, driving the formation of complex 3D networks. The most intensively studied is the *ISO* triblock terpolymer, which provides a comprehensive morphology map based on both experimental data and simulations [18]. The increased block sequence of *ISO* in hydrophilicity prevents the frustration of the A-C interface and the formation of “decorative” phases, like spheres or cylinders on lamellae. This favors the formation of uniform co-continuous network morphology or core-shell structures [19]. Moreover, the amphiphilic nature of ISO (two hydrophobic blocks (I and S) and one hydrophilic block (O)) facilitates the selective incorporation of hydrophilic nanoparticles, thus increasing its utility in various applications. This property makes *ISO* similar to poly (isoprene- b-ethylene oxide) [20], which is extensively used as a structure-directing agent, underscoring the practical and versatile application of *ISO* in materials science.

4. Synthetic Strategies

4.1. Evaporation-Induced Self-Assembly Principle

The Evaporation-Induced Self-Assembly (EISA) protocol utilizes the cooperative self-assembly of block copolymers (BCPs) with specific precursors to create mesoporous architectures through solvent evaporation. In this process, BCP chains interact with soluble precursors, such as carbon sources or metal alkoxides, through intermolecular forces, including hydrogen bonding and electrostatic interactions [21]. As the solvent evaporates, these interactions facilitate the microphase separation of BCPs and precursors, resulting in a continuous network through the condensation or cross-linking of the precursors. These reactions can occur simultaneously with or after the self-assembly phase. Subsequently, the BCP template is typically removed via calcination or solvent extraction, exposing a mesoporous structure. The dimensions of the mesopores and the thickness of the walls are templated by the various blocks of the BCPs, enabling precise control over these features by adjusting the lengths of the sacrificial BCP blocks. As the packing parameter in this system exceeds $p>1$, the formation of bicontinuous mesoporous materials is promoted. These materials are highly valued for their triply periodic minimal surfaces (TPMSs) and the presence of three-dimensional continuous pores, which enable efficient mass transport in multiple directions and optimize the utilization of active sites within the materials. Such attributes are particularly beneficial in energy storage and conversion (ESC) applications, where rapid and unimpeded ion transport is essential.

4.2. Design Strategies for Bicontinuous Mesoporous Structures

Bicontinuous mesoporous structures are typically categorized into three basic types based on their minimal surfaces: the Schoen gyroid (*G*), the Schwarz diamond (*D*), and the Schwarz primitive (*P*) [22], which form two intertwined labyrinths, and are therefore known as: double gyroid (*DG*), double diamond (*DD*), and double primitive (*DP*) structures. They are crucial for applications needing high surface area and structural complexity, making them ideal for advanced ESC applications. In the realm of mesoporous material synthesis using block copolymers, microphase separation often results in three distinct scenarios, depending on the nature of the copolymers (e.g., diblock or triblock of ABA or BAB types) and their interactions with functional precursors, as described below:

4.2.1. Formation of Core-Shell Bicontinuous Phases. In systems where A blocks are associated with a precursor and have a relatively large volume fraction, they usually form a matrix that constitutes the minimal surface area. The B blocks, unassociated with the precursor, form two identical, interpenetrating networks separated by this matrix. This arrangement is ideal for producing ordered bicontinuous porous materials by removing the copolymer template through methods like calcination or solvent extraction, resulting in materials with two sets of interpenetrating pore channels.

4.2.2. Reverse Bicontinuous Phases. When the precursor-associated blocks have a smaller volume fraction compared to the other blocks, the situation reverses. Here, the precursor-associated blocks form two interpenetrating networks, while the other blocks create the surrounding matrix. The removal of the copolymer template in such cases results in bicontinuous porous materials where the two continuous frameworks, initially supported by the polymer matrix, may slightly shift and adhere to one another, forming shifted bicontinuous architectures.

4.2.3. Single Network Bicontinuous Structures. A strategic approach for fabricating bicontinuous structures with a singular network involves utilizing ABC triblock terpolymers, where the A or C block, having a small volume fraction, serves as the structure-directing agent. In such setups, selective interaction of the precursors with the A or C block during phase separation leads to the creation of alternating double networks. Here, the A and C blocks form distinct interconnected networks, with precursors loaded in one, while the B blocks create the matrix that separates these networks. Subsequent removal of the copolymer templates results in bicontinuous porous materials with a single, continuous network. If the A or C block has a large volume fraction, the system acts similarly to the first or second scenario, treating ABC terpolymers like diblocks. These principles clarify the underlying mechanisms governing the formation of various bicontinuous structures and provide a foundation for further discussion and exploration in specific application contexts.

5. Design Challenges

Incorporating mesoporous cathodes within advanced battery designs poses notable challenges due to the complex crystal structures of intercalated compounds and the diversity of cations and anions involved. While the majority of such cathode materials are composed of metal oxides or metal oxide-containing composites, mesoporous carbon and metal oxides have emerged as preferred anode materials. Mesoporous carbons, characterized by their large pore sizes, high surface areas, and excellent electrical conductivity, are particularly advantageous as hosts for large-sized active materials. These properties make mesoporous carbons ideal for loading active materials larger than 2 nm and exhibiting high theoretical capacities, which are essential for alkali metal batteries. Titanium-based oxides, such as TiO_2, are increasingly favoured for their high lithium insertion/extraction operation voltage (1.5–1.8 V versus Li/Li+), which effectively mitigates the formation of solid electrolyte interface (SEI) layers [23]. This characteristic not only ensures enhanced structural stability but also significantly improves the safety profiles of alkali metal batteries. Furthermore, the synthesis of mesoporous Ti-based oxides can be achieved efficiently through block copolymer (BCP) templated synthesis, providing a straightforward route to these structurally advantageous materials. This templating approach enables the creation of well-defined mesoporous architectures, which are essential for optimizing ion transport pathways and enhancing the electrochemical performance of batteries. Constructing a microscopic 3D structure that integrates the anode, electrolyte, and cathode into a unified nanoarchitecture presents significant engineering challenges. Meticulous spatial segregation of anode and cathode networks within the nanostructure is critical to prevent short circuits that could compromise the functionality of the entire device. The electrolyte must facilitate iconic conductivity and prevent electronic contact between the anode and cathode. Traditional fabrication techniques and even advanced deposition methods like atomic layer deposition (ALD) struggle to achieve the necessary precision for continuous 3D nanoarchitectures in battery applications.

6. Conclusion

The exploration of tri-block copolymer-directed self-assembly for synthesizing bicontinuous structures offers a transformative approach in the field of electrical energy storage. The paper shows that these structures have great potential to significantly improve the performance of electrode materials. The bicontinuous structures formed by the self-assembly of tri-block copolymers provide excellent ion channels, leading to improved ion transport and electrochemical properties. The high surface area and ordered mesoporous structure produced by this synthesis method provide numerous active sites for electrochemical reactions, thereby maximizing electrode material utilization. These structures are able to remain stable during cycling by accommodating volume expansion and dispersing mechanical stress, making them well suited for long-term energy storage applications. Furthermore, the flexible design of triblock copolymers allows for precise tuning of pore size and volume to optimize the electrode structure to meet specific battery chemistry and application requirements. Future research should concentrate on scaling the synthesis processes of these copolymers and further optimizing their electrochemical properties to facilitate their transition from laboratory studies to practical applications. Addressing current limitations in processing techniques, including ALD, is critical for the successful integration of these advanced materials into commercial energy storage systems.

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