

ORIGINAL RESEARCH ARTICLE

Recent advances and prospects for highly cobalt nanoparticles embedded in polymer improved strategies for high-rate and durable cobalt-ion batteries storage

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ABSTRACT

Cobalt-ion batteries are considered a promising battery chemistry for renewable energy storage. However, there are indeed challenges associated with co-ion batteries that demonstrate undesirable side reactions due to hydrogen gas production. This study demonstrates the use of a nanocomposite electrolyte that provides stable performance cycling and high Co^{2+} conductivity (approximately 24 mS cm^{-1}). The desirable properties of the nanocomposite material can be attributed to its mechanical strength, which remains at nearly 68 MPa, and its ability to form bonds with H_2O . These findings offer potential solutions to address the challenges of co-dendrite, contributing to the advancement of co-ion batteries as a promising battery chemistry. The exceptional cycling stability of the co-metal anode, even at ultra-high rates, is a significant achievement demonstrated in the study using the nanocomposite electrolyte. The co-metal anode has a 3500-cycle current density of 80 mA cm^{-2} , which indicates excellent stability and durability. Moreover, the cumulative capacity of 15.6 Ah cm^{-2} at a current density of 40 mA cm^{-2} highlights the better energy storage capability. This performance is particularly noteworthy for energy storage applications where high capacity and long cycle life are crucial. The H_2O bonding capacity of the component in the nanocomposite electrolyte plays a vital role in reducing surface passivation and hydrogen evolution reactions. By forming strong bonds with H_2O molecules, the polyethylene helps prevent unwanted reactions that can deteriorate battery performance and efficiency. This mitigates issues typically associated with excess H_2O and ion presence in aqueous Co-ion batteries. Furthermore, the high-rate performance with excellent stability and cycling stability performance (>500 cycles at 8 C) of full $\text{Co}||\text{MnO}_2$ batteries fabricated with this electrolyte further validates its effectiveness in practical battery configurations. These results indicate the potential of the nanocomposite electrolyte as a valuable and sustainable option, simplifying the development of reliable and efficient energy storage systems and renewable energy applications.

Keywords: nanocomposite; cycles; energy storage; battery; polyethylene

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1. Introduction

While nanogel and lithium-ion batteries have made significant advancements, there is ongoing research and development to further improve their performance and address limitations. Some areas of focus include increasing energy density, reducing costs, enhancing safety features, and extending their lifespan. Additionally, other types of advanced energy storage technologies are also being explored alongside lithium-ion batteries. These include solid-state batteries, lithium-sulfur batteries, flow batteries, and various emerging post-lithium-ion technologies. Each of these technologies has its own unique characteristics and potential advantages, such as higher energy

densities, faster charging rates, and increased environmental sustainability. Overall, the development of lithium-ion batteries has revolutionized the field of portable electronics and electric transportation. However, ongoing research and development efforts continue to drive innovation in energy storage technologies, aiming to meet ever-increasing energy demands and accelerate the transition to a more sustainable energy future. One notable advantage of using cobalt as the anode material is its high specific capacity of approximately 820 mAh g⁻¹. Specific capacity refers to the amount of charge that can be stored per unit mass of the electrode material. The high specific capacity of cobalt allows for the storage of a substantial amount of energy in a relatively small amount of material, making it an attractive option for high-capacity battery applications. Additionally, the dissolution and deposition of cobalt ions during charging and discharging, known as cobalt dissolution/deposition, exhibit good reversibility. Reversibility refers to the ability of a battery to efficiently undergo repeated charge and discharge cycles without significant degradation in performance. The reversible dissolution and deposition of cobalt ions contribute to the stable cycling performance of aqueous rechargeable batteries based on cobalt anodes. Furthermore, the use of aqueous nanocomposite electrolytes in these batteries offers potential safety advantages over non-aqueous nanocomposite electrolyte systems, such as those used in LIBs. Aqueous electrolytes are generally less flammable and less prone to thermal runaway reactions, reducing the risk of fire or explosion. This improved safety profile makes aqueous rechargeable batteries with cobalt anodes more appealing for large-scale applications where safety is a critical concern. However, it is important to note that aqueous rechargeable batteries based on cobalt anodes also face challenges. One major challenge is the limited voltage window of aqueous electrolytes compared to non-aqueous electrolytes. This limitation restricts the maximum voltage and energy density that can be achieved in cobalt-based aqueous batteries. Researchers are actively working on addressing these challenges and further improving the performance of aqueous rechargeable batteries based on cobalt anodes. Advances in electrode design, electrolyte formulation, and the development of new materials can contribute to enhancing their energy density, cycle life, and overall performance^[1-4]. One approach is to reduce the content in the H₂O electrolyte, which helps side reactions. This can be achieved through the use of “H₂O-in-salt” in various electrolytes. “H₂O-in-salt” electrolytes involve ultra-high salt concentrations in the electrolytic solution. By increasing the salt concentration, the concentration of free H₂O molecules is reduced, which can mitigate the unwanted side reactions at the cobalt metal anode. This approach has shown promise in improving the reversibility of cobalt plating and stripping processes. Another strategy involves the use of that may be effective as blockers for H₂O molecules. These additives are designed to bind with H₂O molecules, preventing them from interacting with the cobalt metal anode. By minimizing the contact between H₂O and the cobalt surface, the formation of undesirable reaction products can be reduced, leading to improved cycling reversibility. Both of these approaches aim to create an electrolyte environment that promotes reversible cobalt plating and stripping while minimizing side reactions. By reducing the interference of H₂O with the cobalt anode, the performance and cycling stability of aqueous cobalt-ion batteries can be enhanced. It is important to note that electrolyte modification strategies are just one aspect of the overall efforts to optimize aqueous cobalt-ion batteries. Other factors, such as electrode design, interface engineering, and material selection, also play crucial roles in achieving high-performance and durable batteries. Continued research and development in electrolyte engineering, along with advancements in other battery components, will contribute to further improving the cycling reversibility and overall performance of aqueous cobalt-ion batteries^[5-10]. Electrolytes have indeed emerged as a potential solution to address the issue of dendritic growth in aqueous cobalt-ion batteries. These electrolytes offer a denser and more structured environment compared to liquid electrolytes, which can help inhibit the formation and growth of cobalt dendrites during battery operation. Polyethylene, being one of the most abundant biomaterials on earth, has attracted attention as a promising component for electrolytes in cobalt-ion batteries. Polyethylene is a renewable and low-cost material, making it an attractive option for large-scale battery applications. Its inherent biocompatibility and sustainability also contribute to its appeal as a green material. The use of polyethylene in electrolytes helps provide mechanical support and enhanced stability to the battery system. The structure

created by incorporating polyethylene helps to immobilize the cobalt ions and prevents the formation of dendrites, even at high current densities. This improves the cycling stability and safety of aqueous cobalt-ion batteries. Furthermore, polyethylene-based electrolytes offer advantages such as high ionic conductivity, good mechanical strength, and the ability to retain a considerable amount of H₂O. These properties enable efficient ion transport, maintain structural integrity, and promote the desired electrochemical reactions within the battery system. Research and development efforts are actively exploring various approaches to optimize the properties and performance of polyethylene-based electrolytes for aqueous cobalt-ion batteries. This includes the development of composite materials, nanoscale engineering, and the incorporation of other functional additives to further enhance the electrochemical performance and stability of the batteries. By combining the advantages of electrolytes, particularly those based on polyethylene, with other advancements in electrode design, electrolyte chemistry, and system integration, we aim to overcome the challenges associated with dendritic growth and improve the overall performance of aqueous cobalt-ion batteries. Overall, the development of electrolytes, including those based on polyethylene, represents a promising direction in the pursuit of safe, high-performance, and cost-effective energy storage systems for large-scale applications^[11,12]. Polyethylene is a polysaccharide composed of glucose units and is derived from renewable sources such as plants. It exhibits excellent film-forming properties and can be chemically modified to enhance its performance in electrolytes. Explored various approaches to incorporating polyethylene into electrolytes for aqueous cobalt-ion batteries. One common method is to use polyethylene derivatives to form electrolytes. These derivatives can be easily dissolved in H₂O, forming a gel-like structure that immobilizes the electrolyte components. The polyethylene-derived materials provide mechanical support and prevent dendritic growth during battery operation. Moreover, polyethylene can be modified with other functional groups or combined with other polymers to tailor its properties for electrolytes. For example, cross-linking polyethylene with other polymers, such as polyvinyl alcohol (PVA) or poly (acrylic acid) (PAA), can improve the mechanical strength and stability of the nanocomposite electrolyte. The incorporation of polyethylene-based aqueous cobalt-ion batteries offers several advantages. Firstly, these provide a three-dimensional network that enhances the structural integrity of the battery system and inhibits the growth of cobalt dendrites. This feature improves the cycling stability and safety of the battery, allowing for high current densities and longer cycle life.

Additionally, polyethylene exhibits a high H₂O retention capacity, which helps maintain sufficient moisture in the electrolyte and promotes efficient ion transport. This enhances the overall ionic conductivity of the electrolyte and facilitates the electrochemical reactions in the battery. The extensive research on polyethylene-based electrolytes for aqueous cobalt-ion batteries highlights the potential of this material in advancing the performance and safety of these energy storage systems. Further investigations are likely to focus on optimizing the composition, structure, and processing methods of polyethylene-based to unlock their full potential for large-scale applications^[13-28].

The combination of nanopolyethylene and polyethylene results in dense, solid electrolytes, which may serve as the separator for the battery. The addition of polyethylene derivatives, which are abundant, enhances the properties of the electrolyte. The polyethylene creates bonding interactions stronger with H₂O molecules associated with polyethylene. As a result, the electrolyte exhibits lower free H₂O content, which helps minimize detrimental side reactions and improve the stability of the battery system. The incorporation of polyethylene into the relatively rigid network forms a dense structure that contributes to the mechanical strength of the electrolyte. This enables the electrolyte to withstand mechanical stresses during battery operation and prevents the formation of dendrites, enhancing the cycling stability and safety of the cobalt-ion batteries. Furthermore, the nanopolyethylene component in the electrolyte offers high ionic conductivity, facilitating the transport of cobalt ions within the battery. The combination of high ionic conductivity and low free H₂O content promotes efficient ion transport, allowing for high-rate charging and discharging capabilities in the cobalt-ion batteries. Overall, the nanocomposite electrolyte described in this work demonstrates the potential to address some of

the key challenges in aqueous cobalt-ion batteries. Its high ionic conductivity and low free H₂O content improved mechanical strength and contributed to improved battery performance, enabling both high-rate operation and long cycle life. The utilization of commercially available polyethylene and its inexpensive derivative also enhances the cost-effectiveness and scalability of this approach. Further research and development in this area could lead to advancements in aqueous cobalt-ion battery technology and contribute to the development of sustainable and high-performance energy storage systems^[29,30].

This novel work has demonstrated that the use of a nanocomposite electrolyte can support the free H₂O content of a membrane, thereby addressing the issue of extra H₂O side reactions. By increasing the bound H₂O content, the electrolyte promotes cobalt-ion conductivity, which is crucial for efficient battery performance. The presence of bound H₂O within the nanocomposite electrolyte enhances the ionic conductivity by providing a favorable environment for the transport of cobalt ions. This promotes the efficient movement of ions within the battery, contributing to the overall performance and rate capability of the aqueous cobalt-ion battery system. Simultaneously, the increased bound H₂O content also prevents excess free H₂O molecules from participating in undesired reactions. By reducing the availability of H₂O, the likelihood of detrimental reactions, such as unwanted chemical reactions or the formation of hydrogen gas, is minimized. This helps maintain the stability and longevity of the battery system. Furthermore, it could be found that a facile KOH treatment can further enhance the mechanical properties of the nanocomposite electrolyte. This treatment increases the electrolyte universal tensile (universal AGX-V series strength model) to over 68 MPa. The improved tensile strength makes the electrolyte more robust and able to withstand mechanical stresses during battery operation. This is important for maintaining the integrity of the electrolyte and preventing leakage or structural damage that could affect battery performance and safety. The combination of enhanced cobalt ion conductivity, reduced free H₂O content, and improved mechanical strength through KOH treatment demonstrates the potential of the nanocomposite electrolyte for high-performance aqueous cobalt-ion batteries, as shown in **Figure 1**. These findings contribute to the development of electrolytes with desirable properties that enable long cycle life, high-rate capability, and improved overall performance in cobalt-ion battery systems. Further research and development in this area could explore additional treatment methods, material modifications, and characterization techniques to optimize the performance and stability of the nanocomposite electrolyte for aqueous cobalt-ion batteries.

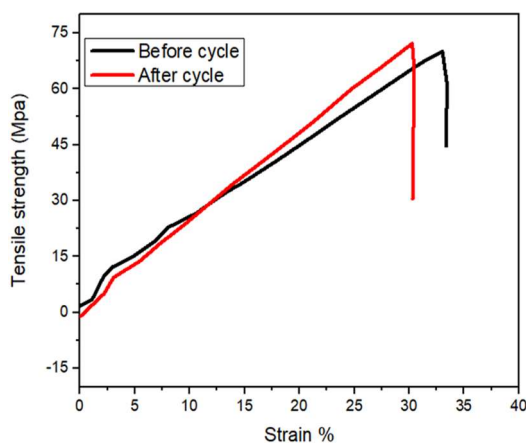


Figure 1. Tensile tests of the composite material before and after 3400 Co||Co cycles at 80 mA/cm².

The nanocomposite electrolyte developed in this novel work exhibits remarkable properties that make it a promising candidate for next-generation energy storage applications. The nanocomposite electrolyte demonstrates a higher cobalt material and better conductivity, rounding off to 24 mS cm⁻¹. This high conductivity enables efficient transport of cobalt ions within the battery, promoting excellent stripping and electroplating of cobalt at the anode side. Stable Co electroplating/stripping current densities remain higher.

The nanocomposite electrolyte allows stable stripping/electroplating remains parallel and cobalt electroplating on the cobalt anode. This indicates the electrolyte's ability to support high-rate charging and discharging, which is critical for applications that require rapid energy storage and retrieval.

Reduction of detrimental side reactions: The existence of H₂O molecules in the electrolyte can lead to hydrogen evolution reactions. The nanocomposite electrolyte significantly reduces these side reactions, contributing to improved stability and long-term cyclability of the battery. A Co||MnO₂ full battery based on the nanocomposite electrolyte demonstrates excellent cyclability, for the 500 cycles achieved at 8 C. This highlights the long cycle life and durability of the battery system, making it suitable for practical applications. The sustainable composition and processing of the nanocomposite electrolyte require minimal effort and are composed of fundamentally biodegradable materials. Its excellent performance and use of biodegradable materials highlight its potential for commercialization and its contribution to the development of cost-effective and sustainable. It does not contain synthetic additives derived from different resources for fossil fuels, further emphasizing its possible as a very sustainable, low-cost potential, and electrolyte is environmentally friendly for the purpose of different energy storage technologies in the current era.

2. Results and discussion

2.1. Material characterization

We have observed that the electrochemical window of the nanocomposite electrolyte shows noteworthy changes after the KOH proper treatment. This indicates that all remaining KOH was effectively rinsed away, and the treatment did not introduce any detrimental effects on the electrochemical stability of the electrolyte. This is an important aspect, as it ensures the electrolyte can maintain its integrity and electrochemical performance during battery operation. Though the KOH did suggestively enhance the mechanical strength of the polyethylene-based membrane, this improvement in mechanical strength is crucial for preventing perforation or damage caused by the growth of cobalt dendrites during battery cycling. The strengthened membrane can withstand the mechanical stress exerted by the dendrites, thereby maintaining the structural integrity of the battery system and preventing short circuits or other safety hazards. The polyethylene-based membrane is a key advantage offered by the KOH treatment. It contributes to the overall stability and safety of the battery, enabling long cycle life and reliable performance. The results of this work demonstrate that the KOH treatment provides a practical and effective method to improve nanocomposite electrolyte (S1). This treatment step can help address one of the critical challenges in aqueous cobalt-ion batteries, which is the prevention of cobalt dendrite-induced damage to the battery components.

Further optimization of the treatment conditions can potentially lead to even greater improvements in the mechanical strength of the polyethylene-based membrane, offering enhanced resistance against dendritic growth and ensuring the long-term durability of aqueous cobalt-ion batteries. The achieved tensile strength of the KOH polyethylene membranes is noteworthy, as it either surpasses or reaches comparable levels to other electrolytes reported in the literature. This indicates that the treatment effectively enhances the mechanical strength of the polyethylene-based membrane, making it suitable for resisting damage caused by cobalt dendrites and other mechanical stresses experienced during battery operation. The substantial improvement in tensile strength observed in the wet state is particularly significant for aqueous cobalt-ion batteries, as they operate in the presence of moisture. The enhanced mechanical strength of the treated membranes helps maintain the structural integrity of the battery system and prevents issues such as dendrite-induced perforation or short circuits.

By achieving a tensile strength of 72 ± 5 MPa, the KOH-treated polyethylene membranes demonstrate their potential as robust and mechanically resilient separators and electrolytes for high-performance energy storage applications. The superior mechanical properties contribute to the overall stability and safety of the battery,

allowing for extended cycle life and reliable performance. Continued research in this area could focus on further optimizing the KOH treatment process to enhance the mechanical strength of the polyethylene-based membranes and explore their compatibility with other battery components. This can contribute to the advancement of aqueous cobalt-ion batteries and their potential utilization in various energy storage applications^[31–33]. Understanding the molecular changes and structural transformations in polyethylene-based membranes is crucial for optimizing their properties and performance. Further research can explore the effects of varying treatment conditions and polyethylene derivatives on the resulting molecular structures and mechanical properties, enabling the development of tailored polyethylene-based membranes for specific applications in energy storage and beyond.

The transference number represents the fraction of total current carried by a specific ion species during electrolysis. The results showed that the transference number of the nanocomposite (0.39) electrolyte was partially higher than that of the glass fiber separator and the aqueous (0.33) electrolyte. This finding implies that the dissociation of Co^{2+} ions in the nanocomposite electrolyte occurs. The transference numbers indicate that the Co^{2+} ions are mobile and participate in the conduction of electric current. The slightly higher transference number in the nanocomposite electrolyte suggests that the Co^{2+} ions experience a comparable environment to that of bulk H_2O , indicating that they are fully solvated in the membrane.

Based on this observation, it is hypothesized that ion conduction in the nanocomposite electrolyte may be formed by H_2O corresponding to the polyethylene. The presence of these H_2O -coordinated channels likely facilitates the movement of Co^{2+} ions through the electrolyte, contributing to its ionic conductivity. However, further studies confirm the exact structure and mechanisms of ion conduction in the polyethylene electrolyte. Additional characterization techniques and molecular modeling approaches can provide deeper insights into the arrangement of H_2O molecules, the role of polyethylene, and the nature of Co^{2+} solvation in the electrolyte, as shown in **Figure 2**. These investigations will help elucidate the underlying mechanisms responsible for the observed ionic conductivity and further optimize the design and performance of nanocomposite-based electrolytes for aqueous cobalt-ion batteries.

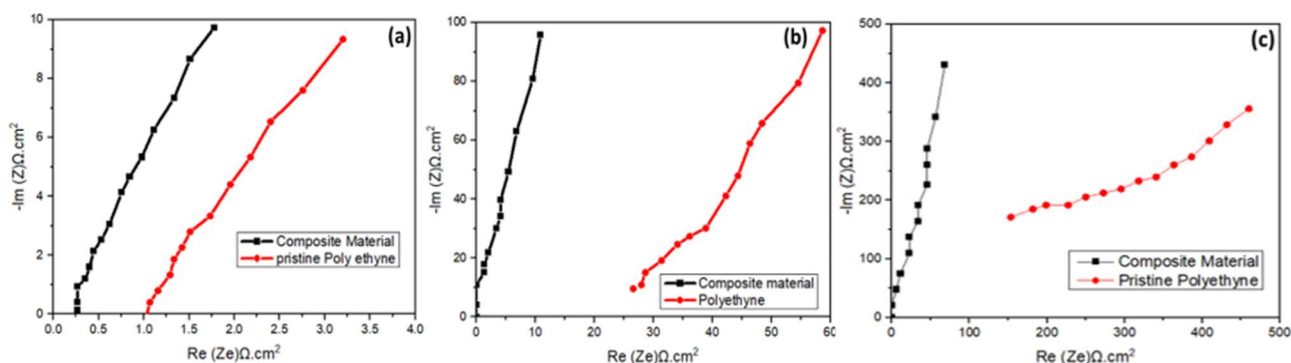


Figure 2. EIS of the composite material (a) wet measurement (b) squeeze using 0.7 MPa pressure (c) placed for a 25 s after squeeze-dry.

Continued research in this area will advance our understanding of ion transport in nanocomposite-based electrolytes and contribute to the development of high-performance and sustainable energy storage technologies.

2.2. Electrodeposition and stripping of Co

The experiment described involves testing the electrodeposition and stripping performance of cobalt in symmetric cells fabricated with different electrolytes and separators. One cell uses a composite electrolyte with a $\text{Co}||\text{Co}$ configuration, while the other cell consists of 2 m CoSO_4 in deionized H_2O . Both cells were subjected to cycling conditions where the current density remained constant at 10 mA cm^{-2} and 5 mAh cm^{-2} of capacity

density for a total of 50 cycles. The purpose of this experiment is likely to compare the performance and morphology of Co electrodeposition and stripping in the two different cell configurations. By using different electrolytes and separators, the impact of these variables on the electrochemical behavior and the resulting Co electrodeposits can be evaluated.

To obtain further insights and interpretations of the experimental results, it would be necessary to analyze the post-mortem SEM images of the Co foils. The SEM analysis would reveal the morphology, uniformity, and potential defects of the electrodeposited Co layers^[34]. Comparing the two cell configurations would help determine if there are any noticeable differences in the quality of the Co electrodeposits. Overall, the experiment provides valuable information about the performance and characteristics of Co electrodeposition and stripping in the given cell configurations, shedding light on the influence of the electrolyte and separator on the electrochemical behavior and morphology of Co deposits. The results of the experiment indicate significant differences in the morphology and crystallographic properties of the electrodeposited cobalt (Co) when using the aqueous electrolyte with a glass fiber separator compared to the nanocomposite electrolyte, as shown in **Figure 3**. This perpendicular growth suggests the formation of dendritic structures, which can be problematic as they can lead to short circuits and reduced performance in batteries and electrochemical devices. On the other hand, when using the nanocomposite electrolyte, the formation of Co platelets in parallel to the Co electrode surface was observed (**Figure 3**). This orientation suggests a more controlled and uniform growth of Co deposits, indicating that the polyethylene electrolyte has the ability to reduce or suppress Co dendrite formation. To further investigate the crystallographic properties of the Co electrodeposits, X-ray diffraction (XRD) measurements were performed on pristine Co and composite material. Previous studies have suggested that this increase in intensity of the (002) peak indicates a preferred growth orientation of Co remains^[34]. These findings suggest that the nanocomposite electrolyte plays a crucial role in controlling the electrodeposition of Co, promoting a desired growth morphology, and reducing the formation of dendritic structures. The XRD results further support the notion that the nanocomposite electrolyte influences the crystallographic orientation of the Co deposits, favoring growth parallel to the electrode surface. These observations have implications for the development of more efficient and stable Co-based batteries or electrochemical systems, as the suppression of dendrite formation can enhance the overall performance and lifespan of such devices^[35,36]. These newly developed heterostructures hold potential for various applications, particularly in energy storage devices and catalysis. The contribution of Co₃O₄ nanoparticles to the system's activity makes them promising candidates for these applications^[34].

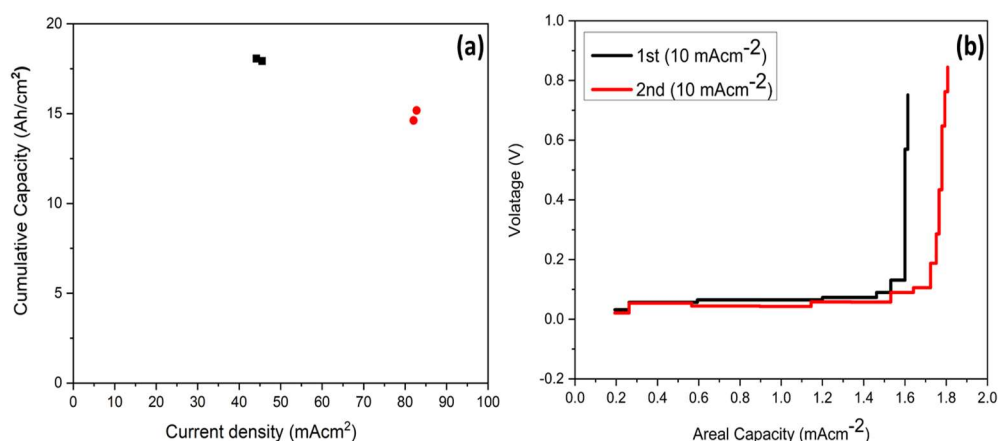


Figure 3. (a) Performance comparison of the Co||Co symmetric cell in terms of the current density and cumulative capacity cycled using the composite material electrolyte (b) The Co stripping/plating of a Co||Cu cell at and 2 mAh cm⁻² and 10 mA cm⁻².

The composition analysis of the Co₃O₄ system was conducted using energy-dispersive X-ray spectroscopy (EDS), and the corresponding spectrum is depicted. The EDS spectrum confirms the presence of

the elements cobalt (Co) and oxygen (O) in the sample, validating the high purity of the samples under investigation. The polyethylene component in the system appears to be completely covered by a dense layer, indicating that only a small contribution of polyethylene is present in the sample already published elsewhere for the electrochemical water splitting process^[34]. This suggests that a substantial amount of polyethylene ensures that the Co₃O₄ nanoparticles are deposited on the polyethylene substrate. This arrangement, where the Co₃O₄ nanoparticles are favorably deposited on polyethylene, is highly beneficial for the Oxygen Evolution Reaction (OER). The presence of a dense layer covering the polyethylene ensures good contact and interaction between the Co₃O₄ nanoparticles and the polyethylene substrate, potentially enhancing the OER activity of the system and being best for energy storage purposes^[34]. The observation of parallel growth is significant because it indicates a more desirable morphology for Co electrodeposits. Parallel growth minimizes the formation of dendritic structures, which can cause short circuits and reduced performance in batteries and other electrochemical devices. By promoting parallel growth, the nanocomposite electrolyte demonstrates its ability to effectively control Co deposition and inhibit the formation of dendrites. This preferred parallel growth, as supported by the results, is important for the development of high-performance Co-based batteries and other electrochemical systems. It suggests that the nanocomposite electrolyte can serve as a promising electrolyte candidate for applications where controlled Co electrodeposition and suppression of dendrite formation are crucial factors for device performance and stability. This lack of mechanical constraint promotes the formation of dendritic structures, as the Co platelets can freely extend and branch out in different directions. On the other hand, the polyethylene membrane used as an electrolyte exhibits high mechanical strength and a dense structure. These properties mechanically restrict the electrodeposition of Co and limit its growth b/w the membrane, the Co foil, and the surface. This mechanical constraint leads to the preferred parallel growth of Co platelets, as observed in the experiment. The mechanical confinement provided by the polyethylene membrane prevents the expansion and branching of Co platelets, thereby inhibiting the formation of dendrites. The parallel growth observed in this configuration suggests a more controlled and confined deposition process. Therefore, in addition to the electrolyte's chemical properties, the mechanical properties and structural characteristics of the separator or membrane play a crucial role in influencing the electrodeposition behavior and morphology of Co. The dense and mechanically strong nature of the polyethylene membrane helps maintain a more uniform and controlled growth of Co, promoting parallel growth and suppressing dendrite formation. The accumulation of Co ions at these regions creates localized areas of higher concentration, resulting in the formation of "hot spots" for electrodeposition. In these hot spots, the electric field strength is higher due to the higher concentration of Co ions, which leads to an accelerated deposition of Co in a perpendicular growth manner. This positive feedback loop, where the deposition of Co enhances the local electric field, further promotes the perpendicular growth of Co platelets. This phenomenon is observed in so many other systems, like lithium-ion batteries. The formation is a significant concern in battery systems as it can lead to short circuits, decreased battery performance, and even safety hazards. Therefore, understanding the factors that contribute to dendrite formation, such as the accumulation of ions in localized regions with higher electric field strength, is crucial for developing strategies to mitigate dendrite growth and improve the stability and safety of electrochemical devices.

In contrast, the nanocomposite electrolyte used in the experiment provides a different environment. Its dense and mechanically strong structure, along with the confinement effect, limits the mobility of Co²⁺ ions. This reduced ion mobility helps to suppress the formation of hot spots and the accumulation of Co ions in rough or defect-prone regions, thereby mitigating the positive feedback loop that promotes dendritic growth. Overall, the ability of the nanocomposite electrolyte to restrict ion mobility and prevent the formation of hot spots contributes to the observed parallel growth of Co platelets and helps suppress dendrite formation^[37]. The presence of polyethylene chains within the nanocomposite electrolyte can promote the formation of hydrogen bonds with H₂O molecules. This bonding may create a more structured environment and enhance the

interaction between H₂O and the polyethylene chains. As a result, the Co ions may migrate along the polyethylene chains, facilitated by the presence of H₂O molecules that are associated with the polyethylene chains. This migration along the polyethylene chains can lead to a more even distribution of Co ions on the Co foil, relative to their accumulation potential “hot spots” as observed in the aqueous electrolyte system. By promoting a more uniform distribution, the nanocomposite electrolyte helps to mitigate the localized concentration gradients that contribute to dendrite formation.

The presence of this passivation layer is likely a result of the reaction between Co ions and the sulfate species which presents in the electrolyte. The formation of this passivation layer can act as a protective barrier, preventing further unwanted reactions between the Co foil and the electrolyte. The passivation layer can contribute to the stability and improved cycling performance of the Co electrode. It helps to minimize side reactions and potential degradation of the Co electrode during cycling. Overall, the nanocomposite electrolyte, through its bonding with H₂O molecules and potential influence on Co ion migration, helps to promote a more uniform distribution of Co ions on the Co foil surface. Additionally, the formation of the Co passivation layer in the aqueous electrolyte contributes to the stability of the Co electrode. These factors are likely to play a role in reducing dendrite formation and improving the performance of Co-based electrochemical systems.

The strong bonding between polyethylene and H₂O molecules helps to maintain a more hydrated environment and limits the interaction between Co ions and sulfate species present in the electrolyte. Consequently, the formation of the Co passivation layer is suppressed, allowing Co to deposit more evenly and uniformly over the entire surface of the Co foil throughout the cycling process. By reducing the formation of the passivation layer and promoting uniform Co deposition, the nanocomposite electrolyte contributes to the suppression of dendritic and perpendicular growth of Co. This suppression enables stable and reversible Co plating and stripping, which are crucial for the performance and cycling stability of Co-based electrochemical systems. The advantages of the nanocomposite electrolyte, including the reduction in Co passivation layer formation and the promotion of uniform Co deposition, play a vital role in suppressing dendritic growth and facilitating stable Co plating and stripping processes. These characteristics contribute to the overall stability and improved electrochemical performance of Co-based systems utilizing the nanocomposite electrolyte^[38]. The initial polarization voltage was significantly higher, starting at 100 mV and increasing after only 30 cycles. This suggests that the electrode/electrolyte interface in this configuration experiences higher resistance and instability, leading to degraded electrochemical performance. The observed difference in polarization voltage behavior between the two electrolytes further emphasizes the superior durability of the Co anode interface when using the nanocomposite electrolyte. The low and stable polarization voltage throughout cycling indicates a more favorable and stable electrochemical environment, contributing to the improved durability of the cell. Furthermore, the visible swelling at 10 mA cm⁻² and 5 mAh cm⁻² after the 160 cycles indicates physical changes and degradation in the electrode or separator materials. This swelling is likely a result of increased volume expansion and gas evolution, which can be attributed to the formation of dendritic structures, electrolyte breakdown, and the accumulation of unwanted side products.

Overall, the comparison of the polarization voltage behavior and the visible swelling between the nanocomposite electrolyte demonstrates the significantly greater durability of the Co anode interface when using the nanocomposite electrolyte. This improved durability is crucial for the long-term stability and reliable performance of Co-based electrochemical systems. The inflation or volumetric swelling observed in the cell with the aqueous electrolyte is likely due to the hydrogen evolution reaction occurring on the Co anode. The absence of such swelling in the cell with the nanocomposite electrolyte indicates a reduced hydrogen evolution reaction, demonstrating the enhanced stability and durability of the nanocomposite electrolyte in preventing unwanted gas evolution and associated cell swelling^[38]. Hydrogen evolution has been a long-standing issue in aqueous Co batteries as it leads to gas evolution, cell swelling, and potential safety concerns. By mitigating this issue, the polyethylene electrolyte offers a solution to improve the stability and reliability of Co-based

battery systems. The strong bonding between the nanocomposite electrolyte and H₂O molecules also contributes to the overall stability and integrity of the electrolyte system. It helps maintain a more structured and controlled environment, reducing the likelihood of unwanted reactions and side effects. Therefore, the strong bonding between the nanocomposite electrolyte and H₂O molecules not only helps to mitigate hydrogen evolution but also enhances the overall performance and safety of aqueous Co batteries. This characteristic makes the nanocomposite electrolyte a promising candidate for addressing one of the key challenges in the development of efficient and reliable Co-based battery technologies. At a current density of 80 mA cm⁻² (4 mAh cm⁻²), the Co-symmetric cells showed remarkable cycling stability, completing 3500 cycles, as shown in **Figure 4**.

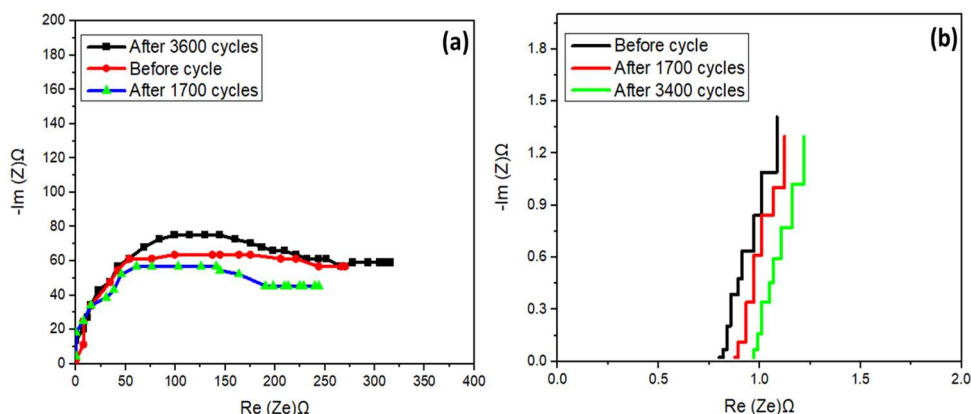


Figure 4. (a) EIS of a Co||Co symmetric cell using the composite material before cycling, after 1700 cycles, and after 3400 cycles, with a current density and capacity density of 80 mA/cm² and 4 mAh, respectively. (b) zoom-in view for the x-intercepts.

These results surpass the performance of previously reported Co symmetric cells utilizing different electrolyte systems, including electrolytes and Co salts with various additives. The nanocomposite electrolyte demonstrates superior capabilities in terms of current density and cumulative plating capacity. The ability to achieve such high current densities and cumulative plating capacities showcases the potential of the electrolyte for the nanocomposite for enabling fast discharging/charging of Co-based anodes. This is a significant advancement in the field of Co based battery technologies, as it opens up possibilities for high-power applications that require rapid charging and discharging capabilities.

The initial decrease in polarization and interfacial resistance can be attributed to the formation and stabilization of the electrode-electrolyte interface during the initial cycles. As the cell operates and undergoes cycling, the interface gradually evolves and adapts to the electrochemical reactions and stresses involved in the system. After a certain number of cycles (in this case, around 1700 cycles), the interfacial resistance begins to increase. This increase in resistance suggests changes or degradation in the electrode-electrolyte interface, potentially caused by the accumulation of reaction byproducts, degradation of the electrolyte, or other factors that affect the ionic and electronic transport at the interface. The subsequent increase in polarization voltage aligns with the increase in interfacial resistance. As the resistance at the electrode-electrolyte interface rises, it becomes more challenging for charge transfer processes to occur smoothly, resulting in an increased polarization voltage.

Electrochemical Impedance Spectroscopy (EIS) measurements provide valuable information about electrochemical processes and interfacial behavior. By conducting EIS measurements at different stages of cycling (beginning, after 1700 cycles, and after 3400 cycles), the changes in interfacial resistance can be tracked, and insights into the evolution of the electrode-electrolyte interface over time can be gained, as shown in **Figure 5**. The dynamic behavior of polarization and interfacial resistance during cycling indicates the complexity of the electrochemical processes and the need for further investigation to understand the underlying mechanisms. Additional analysis and characterization techniques may be required to identify the specific

factors contributing to the changes in interfacial behavior and polarization voltage during cycling with the nanocomposite electrolyte. Overall, the observation of the polarization decrease followed by an increase, as well as the corresponding changes in interfacial resistance, indicates the dynamic nature of the electrode-electrolyte interface in the Co-symmetric cells using the nanocomposite electrolyte. This behavior highlights the need for further research to elucidate the factors influencing the interface dynamics and develop strategies to optimize the stability and performance of the electrode-electrolyte system, as shown in **Figure 6**.

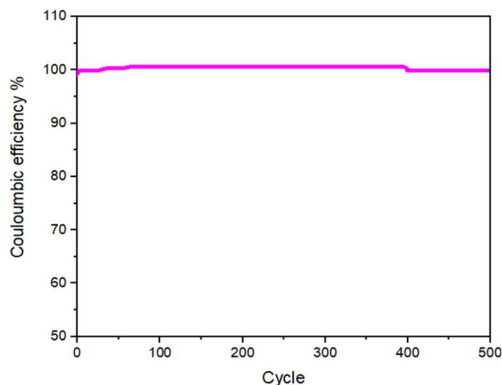


Figure 5. Coulombic efficiency of the Co||Co asymmetric cell using the composite material at 10 mA/cm² and 2 mAh/cm². The fluctuation during >400 cycles is likely due to the inevitable dendrite formation on Cu, although it is already suppressed comparing to aqueous electrolyte.

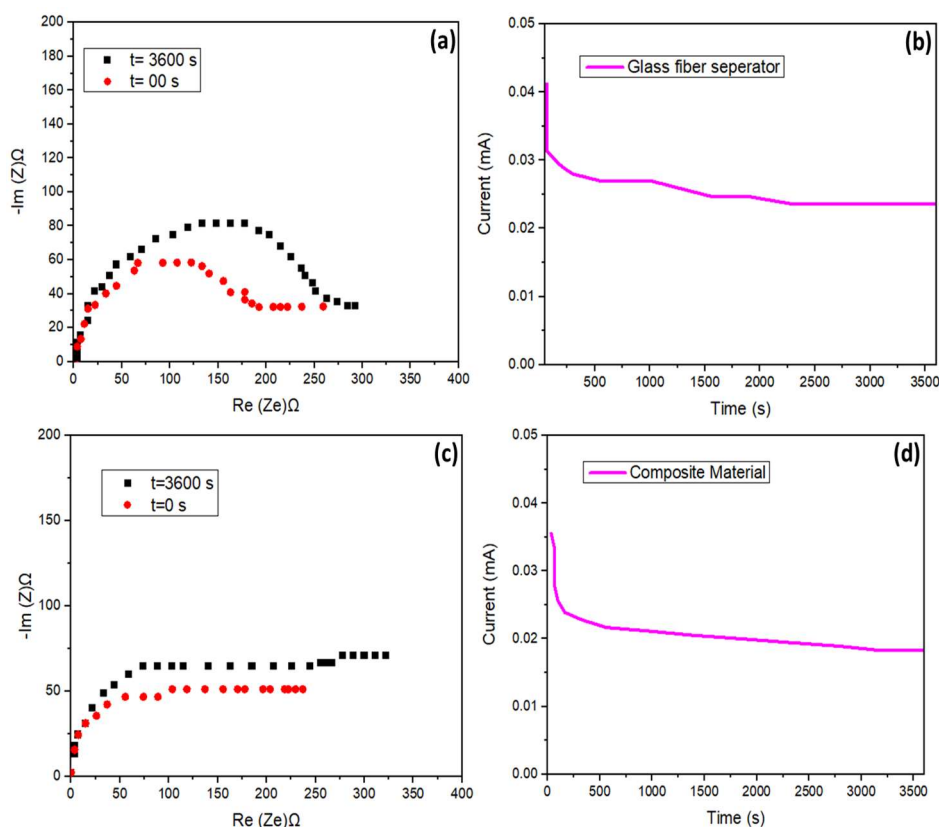


Figure 6. (a) EIS of the glass fiber separator the DC polarization curves with 10 mV; (b) glass fiber separator; (c) Composite material; (d) Composite electrolyte.

This passivation layer can impede the electrochemical reactions and increase the polarization voltage. The gradual formation and accumulation of this passivation layer over time may contribute to the increasing polarization observed in the later stages of cycling. Furthermore, the comparison of the EIS spectra provides insights into the bulk resistivity and ionic conductivity of the electrolyte. The increase in bulk resistivity after cycling indicates a decrease in bulk ionic conductivity, likely due to the feeding of H₂O cycling. As the cycling

progresses, the bound H₂O within the nanocomposite electrolyte may become depleted, leading to a reduction in the availability of mobile ions and a subsequent decrease in bulk ionic conductivity. These explanations align with the dynamic nature of the electrode-electrolyte interface and the evolving interfacial behavior observed during cycling. The initial activation, the formation of the passivation layer, and the consumption of bound H₂O collectively contribute to the observed changes in interfacial resistance, polarization, and bulk resistivity. These phenomena aid in the development of strategies to optimize the performance and stability of the Co symmetric cells using the nanocomposite electrolyte. The observed evolution of interfacial resistance, polarization, and bulk resistivity during cycling can be attributed to interfacial activation, the formation of passivation layers, and the consumption of bound H₂O. Understanding these dynamics is crucial for the further improvement and optimization of Co-based battery systems using the nanocomposite electrolyte. At a capacity of 2 mAh cm⁻² a current density of 10 mA cm⁻², and 0.8 V (cut-off voltage), the Co||Cu cell performance was assessed. However, the specific results or observations for this asymmetric cell were not provided in the given information.

To further analyze the performance of the Co||Cu cell and draw conclusions about the electrodeposition of Co on Cu foil using the nanocomposite electrolyte, it would be helpful to have access to the data or specific findings presented in **Figure 6** or other relevant figures or information. If additional details or specific results from **Figure 6** can be provided, it would be happy to provide further assistance in understanding and discussing the electrodeposition behavior and performance of the Co||Cu asymmetric cell using the nanocomposite electrolyte. The excellent efficiency of charge and discharge processes in the Co||Cu cell, as shown in **Figure 5**, This high Coulombic efficiency indicates minimal loss of charge during cycling, emphasizing the stability and reliability of the Co-Cu foil deposition with the nanocomposite electrolyte. Additionally, the smaller voltage of 105 mV further highlights the efficient charge-discharge behavior of the Co||Cu cell. The reduced voltage hysteresis implies improved energy efficiency and lower energy losses during cycling. This characteristic is crucial for achieving high overall efficiency and stable performance in Co-based battery systems. Taken together, these results demonstrate the promising potential of the nanocomposite electrolyte for the electrodeposition of Co on Cu foil in Co||Cu asymmetric cells. The high Coulombic efficiency and reduced voltage hysteresis indicate the stability, efficiency, and overall performance of the Co||Cu cell using the nanocomposite electrolyte. Indeed, the successful performance of both the Co||Co and Co||Cu cells using the polyethylene electrolyte highlights its better cyclability, stability, and capability at a higher current density. These characteristics are crucial for the development of high-power density aqueous cobalt-ion batteries. The stability and cyclability demonstrated by the Co||Co cell indicate the electrolyte's ability to support repeated cycles of Co plating and stripping without significant degradation. This is a key requirement for long-term and reliable battery operation. Furthermore, the capability of the nanocomposite electrolyte to remain at higher current densities is vital for achieving a high density of power in cobalt-ion batteries. The ability to deliver and extract charge at high rates is essential for applications that require rapid charging and discharging, such as electric vehicles and grid energy storage systems. By demonstrating stability, cyclability, and high current density performance in both Co||Co and Co||Cu cells, the nanocomposite electrolyte exhibits great potential for enabling high-density aqueous cobalt-ion batteries. These results contribute to advancing the development of Co-based battery technologies and offer promising solutions for energy storage applications that demand high performance and power density. Overall, the capability of the nanocomposite electrolyte to deliver higher cyclability, stability, and high current density provides a solid foundation for the development of high-power density aqueous cobalt-ion batteries.

2.3. Co||MnO₂ full cell performance

By casting the synthesized MnO₂ nanorods onto carbon paper, a conductive and porous substrate, the resulting cathode provides a high surface area and facilitates efficient charge transfer during electrochemical reactions. Using this Co||MnO₂ configuration, the performance of the nanocomposite electrolyte can be

evaluated in full cells. The nanocomposite electrolyte serves as the bridge between the Co anode and the MnO₂ cathode, facilitating the ionic conductivity and enabling the electrochemical reactions to occur. The evaluation of the polyethylene electrolyte in full cells with Co||MnO₂ chemistry allows for an assessment of its compatibility, stability, and overall performance within the specific battery system. This information is crucial for understanding how the nanocomposite electrolyte can contribute to the development of high-performance and reliable Co-based battery technologies. For more detailed results and insights regarding the performance of the nanocomposite electrolyte in these full cells, please refer to the specific findings presented in the associated references, such as reference^[39]. In the Co||MnO₂ full cell using the nanocomposite electrolyte, the mass loading of MnO₂ was approximately 6 mg cm⁻². This indicates the amount of MnO₂ material present on the carbon paper cathode per unit area. The performance of the Co||MnO₂ full cell was evaluated in terms of discharge and charge capacities at a high rate of 8 C, where 1 C corresponds to a current of 250 mA per gram of MnO₂. According to **Figure 7**, the Co||MnO₂ cell exhibited a discharge/charge capacity of approximately 200 mAh g⁻¹. This result suggests that the Co||MnO₂ full cell using the nanocomposite electrolyte can deliver and extract charge rapidly, enabling efficient energy storage and retrieval even at high current rates. The high discharge/charge capacity at 8 C indicates the suitability of the nanocomposite electrolyte for high-power applications where quick energy delivery or rapid charging is required. These findings demonstrate the potential of the nanocomposite electrolyte in facilitating the high-performance operation of Co||MnO₂ full cells. The combination of the nanocomposite electrolyte, MnO₂ cathode, and Co anode offers promising prospects for the development of advanced Co-based battery systems with high power density and reliable performance. For more detailed information regarding the performance characteristics and behavior of the Co||MnO₂ full cell with the nanocomposite electrolyte, including other discharge/charge rates or cycling performance, please refer to the associated reference or relevant figures provided in the supporting information. In the Co||MnO₂ full cell with the nanocomposite electrolyte, an impressive 95% capacity was attained after 500 cycles, as shown in **Figure 7**. This indicates that the battery maintained a significant portion of its initial capacity even after prolonged cycling. The high-capacity retention is indicative of the excellent cycling stability and durability of the Co||MnO₂ full cell using the nanocomposite electrolyte. It suggests that the electrolyte effectively supports stable electrochemical reactions and preserves the integrity of the electrode materials, enabling sustained performance over multiple charge-discharge cycles. Moreover, the absence of short-circuits during high-rate cycling further demonstrates the inhibitory effect of the polyethylene electrolyte on dendritic growth. Dendritic growth refers to the formation of undesirable needle-like structures that can lead to internal short circuits and degrade the performance and safety of the battery. The ability of the nanocomposite electrolyte to inhibit dendritic growth is crucial for maintaining the integrity of the cell and ensuring its reliable operation over extended cycles. The combination of the high-capacity retention and the absence of short-circuits confirms the effectiveness of the nanocomposite electrolyte in enhancing the stability, safety, and cycling performance of the Co||MnO₂ full cell. These results highlight the potential of the nanocomposite electrolyte for the development of advanced Co-based battery systems with long cycle life, high-capacity retention, and improved safety characteristics. For further insights into the performance and behavior of the Co||MnO₂ full cell using the nanocomposite electrolyte, including additional cycling data or specific mechanisms underlying the inhibitory effect on dendritic growth, please refer to the associated reference or relevant figures in the supporting information. The rate performance of the Co||MnO₂ battery using the nanocomposite electrolyte is indeed remarkable, as evidenced by both the discharge profile and cycling performance. In terms of the discharge profile (**Figure 7**), the battery exhibits excellent rate capability, delivering high discharge capacities at various current rates. At 1 C (where 1 C corresponds to a current of 250 mA/g of MnO₂), the battery achieves a discharge capacity of 284 mAh g⁻¹. As the discharge rate increases to 2 C, 4 C, and 8 C, the battery still demonstrates impressive discharge capacities of 256, 228, and 199 mAh g⁻¹, respectively. This indicates the ability of the battery to deliver significant amounts of charge even at high current rates, highlighting its suitability for applications that demand rapid energy release. Furthermore, the

cycling performance (**Figure 7**) of the Co||MnO₂ battery is excellent, as it maintains a stable and high discharge capacity over multiple cycles. This indicates the battery's ability to sustain its performance and capacity retention during extended cycling. The stable discharge capacities achieved at different current rates throughout the cycling process demonstrate the durability and reliability of the battery, making it suitable for long-term and demanding applications and delivering discharge capacities of 282, 256, 228, and 199 mAh g⁻¹ at 1, 2, 4, and 8 C. These characteristics, in terms of discharge and cycling response, highlight the effectiveness of the nanocomposite electrolyte in facilitating efficient charge transfer, maintaining stable electrochemical reactions, and preserving the capacity of the Co||MnO₂ battery. These results underscore the potential of the nanocomposite electrolyte in advancing the development of high-performance Co-based battery systems with exceptional rate capabilities and cycling stability. The ability of the Co||MnO₂ battery using the nanocomposite electrolyte to maintain a high discharge capacity of 16 C at a high rate is impressive. At this high discharge rate, the battery still delivers a substantial discharge of 168 mAh g⁻¹. This demonstrates the exceptional rate capability and fast charge-discharge kinetics facilitated by the nanocomposite electrolyte. The discharge capacity at 16 C indicates that the battery can efficiently store and release a significant amount of energy within a short period of time. Achieving such high discharge capacities at extremely high rates is crucial for applications that require rapid energy delivery or rapid charging, such as electric vehicles and other high-power devices. The ability of the Co||MnO₂ battery with the nanocomposite electrolyte to perform reliably at such high rates expands its potential for demanding and high-performance applications. The comparison of the cycling performance between the nanocomposite electrolyte and other electrolyte systems provides valuable insights into the superiority of the polyethylene electrolyte and its compatibility with the Co||MnO₂ chemistry. When comparing the nanocomposite electrolyte with the polyethylene-only electrolyte (0% polyethylene) and the H₂O electrolyte/glass fiber separator, the nanocomposite electrolyte demonstrates the best performance in terms of cycling stability. The specific results and data can be referred to in **Figure 8**.

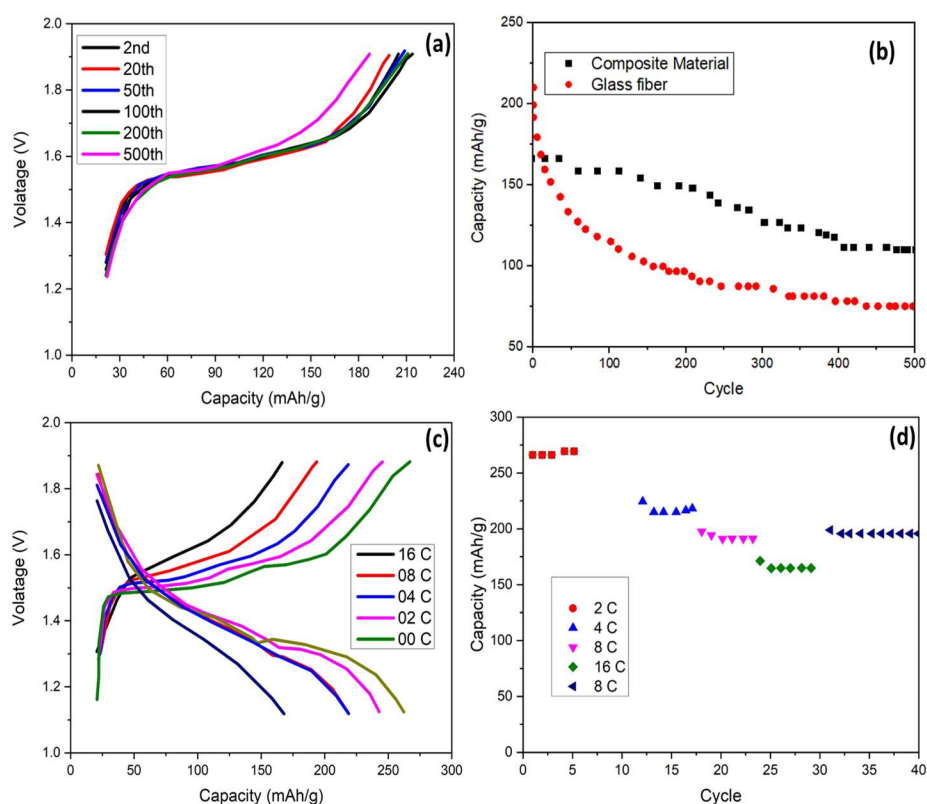


Figure 7. Electrochemical performance of Co||MnO₂ full cells using the composite material **(a)** Galvanostatic charge/discharge of the Co||MnO₂ cell at 8 C cell potential. **(b)** The coulombic and Capacity of Co||MnO₂ cell at 8 C using electrolyte. **(c)** Galvanostatic potential for the charge/discharge Co||MnO₂ cell at various scanning rates. **(d)** The Co||MnO₂ cell rate performance at 1 C to 16 C.

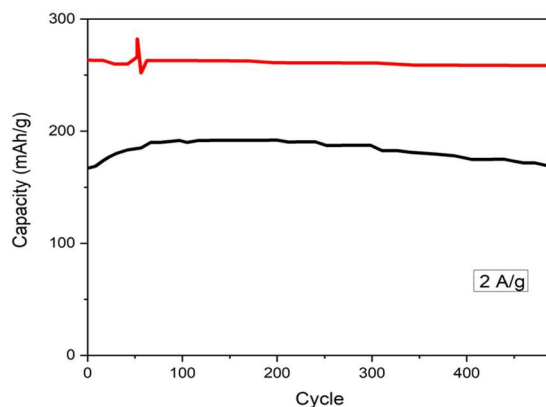


Figure 8. Cycling performances of Co||MnO₂ cells made using the composite material in electrolyte for the separator of glass fiber at 8 C.

3. Conclusion

This robust work has successfully demonstrated the brilliant and self-explanatory results obtained from the incorporation of a nanocomposite electrolyte material into aqueous media for cobalt-ion batteries. The combination of the low-cost, accessible natural materials and the facile fabrication process highlights the potential of the nanocomposite electrolyte as a cost-effective solution for aqueous cobalt-ion batteries and other energy storage applications. Overall, this work showcases the development of a nanocomposite electrolyte that not only delivers excellent battery performance but also emphasizes the importance of sustainable and environmentally friendly materials and fabrication methods. These findings contribute to the ongoing efforts to create more sustainable and economically viable energy storage technologies. The nanocomposite electrolyte with 5 wt% polyethylene, as described in the work, exhibits an impressive range of properties and performance in the context of cobalt-ion batteries. Indicating its robustness and ability to withstand mechanical stresses during battery operation. This mechanical strength helps prevent damage, including dendrite formation, and contributes to the long-term stability of the battery. Excellent H₂O bonding and ionic conductivity. The effective bonding of H₂O molecules contributes to high ionic conductivity, enabling efficient transport of cobalt ions within the battery. The ability to achieve ultra-fast electroplating/stripping of cobalt at high current densities without dendrite formation is a significant advantage for long-term battery stability and safety. Excellent cyclability and rate performance: Co||MnO₂ cells. The nanocomposite electrolyte demonstrates exceptional cyclability, retaining 95% of its capacity at 8 C after 500 cycles. Additionally, the performance is very impressive, with a strong capability of up to 16 C. These characteristics highlight the stability, durability, and fast-charging capabilities of the battery system. Facile fabrication and compatibility with Co||MnO₂ chemistry: The fabrication process of the nanocomposite electrolyte is straightforward and can be easily scaled up. Moreover, the electrolyte exhibits excellent compatibility with Co||MnO₂ chemistry, a common and widely used system in cobalt-ion batteries. Its combination of low cost, sustainability, ease of fabrication, exceptional electrochemical performance, and compatibility with existing battery chemistries makes it a promising candidate for advancing the development of large-scale energy storage systems. Continued research and development efforts in this area can further optimize the nanocomposite electrolyte and pave the way for its practical application in the field of energy storage.

Author contributions

Conceptualization, AQM; methodology, AQM; software, NAM; formal analysis, NS; investigation, NAM and AAB; resources, MIC; data curation, MIC; writing—original draft preparation, AAB and MIC; writing—review and editing, AQM; visualization, AAJ; supervision, AAB; project administration, AQM. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

All authors declare no conflict of interest.

References

1. Du Y, Xu Y, Zhang Y, et al. Metal-organic-framework-derived cobalt-vanadium oxides with tunable compositions for high-performance aqueous zinc-ion batteries. *Chemical Engineering Journal* 2023; 457: 141162. doi: 10.1016/j.cej.2022.141162
2. Zhao X, Mao L, Cheng Q, et al. Interlayer engineering of preintercalated layered oxides as cathode for emerging multivalent metal-ion batteries: Zinc and beyond. *Energy Storage Materials* 2021; 38: 397–437. doi: 10.1016/j.ensm.2021.03.005
3. Chuhadiya S, Himanshu, Suthar D, et al. Metal organic frameworks as hybrid porous materials for energy storage and conversion devices: A review. *Coordination Chemistry Reviews* 2021; 446: 214115. doi: 10.1016/j.ccr.2021.214115
4. Hu H, Guan B, Lou X. Construction of complex CoS hollow structures with enhanced electrochemical properties for hybrid supercapacitors. *Chem* 2016; 1(1): 102–113. doi: 10.1016/j.chempr.2016.06.001
5. Ma C, Yang K, Zhao S, et al. Recyclable and ultrafast fabrication of zinc oxide interface layer enabling highly reversible dendrite-free Zn anode. *ACS Energy Letters* 2023; 8(2): 1201–1208. doi: 10.1021/acscenergylett.2c02735
6. Chen CY, Matsumoto K, Kubota K, et al. A room-temperature molten hydrate electrolyte for rechargeable zinc-air batteries. *Advanced Energy Materials* 2019; 9(22): 1900196. doi: 10.1002/aenm.201900196
7. Wang F, Borodin O, Gao T, et al. Highly reversible zinc metal anode for aqueous batteries. *Nature Materials* 2018; 17(6): 543–549. doi: 10.1038/s41563-018-0063-z
8. Yang H, Chang Z, Qiao Y, et al. Constructing a super-saturated electrolyte front surface for stable rechargeable aqueous zinc batteries. *Angewandte Chemie International Edition* 2020; 59(24): 9377–9381. doi: 10.1002/anie.202001844
9. Naveed A, Yang H, Yang J, et al. Highly reversible and rechargeable safe Zn batteries based on a triethyl phosphate electrolyte. *Angewandte Chemie International Edition* 2019; 58(9): 2760–2764. doi: 10.1002/anie.201813223
10. Wang N, Yang Y, Qiu X, et al. Stabilized rechargeable aqueous zinc batteries using ethylene glycol as water blocker. *Chemistry Sustainability Energy Materials* 2020; 13(20): 5556–5564. doi: 10.1002/cssc.202001750
11. Ding Y, Pang Z, Lan K, et al. Emerging engineered wood for building applications. *Chemical Reviews* 2022; 123(5): 1843–1888. doi: 10.1021/acs.chemrev.2c00450
12. Dong Q, Zhang X, Qian J, et al. A cellulose-derived supramolecule for fast ion transport. *Science Advances* 2022; 8(49): eadd2031. doi: 10.1126/sciadv.add2031
13. Yang Z, Li W, Zhang Q, et al. A piece of common cellulose paper but with outstanding functions for advanced aqueous zinc-ion batteries. *Materials Today Energy* 2022; 28: 101076. doi: 10.1016/j.mtener.2022.101076
14. Zhou J, Zhang R, Xu R, et al. Super-assembled hierarchical cellulose aerogel-gelatin solid electrolyte for implantable and biodegradable zinc ion battery. *Advanced Functional Materials* 2022; 32(21): 2111406. doi: 10.1002/adfm.202111406
15. Ma L, Chen S, Wang D, et al. Super-stretchable zinc-air batteries based on an alkaline-tolerant dual-network hydrogel electrolyte. *Advanced Energy Materials* 2019; 9(12): 1803046. doi: 10.1002/aenm.201803046
16. Xu W, Liu C, Wu Q, et al. A stretchable solid-state zinc ion battery based on a cellulose nanofiber—Polyacrylamide hydrogel electrolyte and a $Mg_{0.23}V_2O_5 \cdot 1.0H_2O$ cathode. *Journal of Materials Chemistry A* 2020; 8(35): 18327–18337. doi: 10.1039/D0TA06467J
17. Fu J, Wang H, Xiao P, et al. A high strength, anti-corrosion and sustainable separator for aqueous zinc-based battery by natural bamboo cellulose. *Energy Storage Materials* 2022; 48: 191. doi: 10.1016/j.ensm.2022.02.052
18. Glatz H, Lizundia E, Pacifico F, Kundu D. An organic cathode based dual-ion aqueous zinc battery enabled by a cellulose membrane. *ACS Applied Energy Materials* 2019; 2(2): 1288–1294. doi: 10.1021/acsaem.8b01851
19. Xu M, Dou H, Zhang Z, et al. Hierarchically nanostructured solid-state electrolyte for flexible rechargeable zinc-air batteries. *Angewandte Chemie International Edition* 2022; 134(23): e202117703. doi: 10.1002/ange.202117703
20. Zhang Y, Chen Y, Li X, et al. Bacterial cellulose hydrogel: A promising electrolyte for flexible zinc-air batteries. *Journal of Power Sources* 2021; 482: 228963. doi: 10.1016/j.jpowsour.2020.228963

21. Zhao N, Wu F, Xing Y, et al. Flexible hydrogel electrolyte with superior mechanical properties based on poly (vinyl alcohol) and bacterial cellulose for the solid-state zinc-air batteries. *ACS Applied Materials & Interfaces* 2019; 11(17): 15537–15542. doi: 10.1021/acsami.9b00758
22. Cao J, Zhang D, Gu C, et al. Modulating Zn deposition via ceramic-cellulose separator with interfacial polarization effect for durable zinc anode. *Nano Energy* 2021; 89: 106322. doi: 10.1016/j.nanoen.2021.106322
23. Zhou W, Chen M, Tian Q, et al. Cotton-derived cellulose film as a dendrite-inhibiting separator to stabilize the zinc metal anode of aqueous zinc ion batteries. *Energy Storage Materials* 2022; 44: 57–65. doi: 10.1016/j.ensm.2021.10.002
24. Liang Y, Ma D, Zhao N, et al. Novel concept of separator design: Efficient ions transport modulator enabled by dual-interface engineering toward ultra-stable Zn metal anodes. *Advanced Functional Materials* 2022; 32(25): 2112936. doi: 10.1002/adfm.202112936
25. Yang P, Li J, Lee SW, Fan H. Printed zinc paper batteries. *Advanced Science* 2022; 9(2): 2103894. doi: 10.1002/advs.202103894
26. Ge X, Zhang W, Song F, et al. Single-ion-functionalized nanocellulose membranes enable lean-electrolyte and deeply cycled aqueous zinc-metal batteries. *Advanced Functional Materials* 2022; 32(26): 2200429. doi: 10.1002/adfm.202200429
27. Cao J, Zhang D, Gu C, et al. Manipulating crystallographic orientation of zinc deposition for dendrite-free zinc ion batteries. *Advanced Energy Materials* 2021; 11(29): 2101299. doi: 10.1002/aenm.202101299
28. Zhang X, Li J, Liu D, et al. Ultra-long-life and highly reversible Zn metal anodes enabled by a desolvation and deanionization interface layer. *Energy & Environmental Science* 2021; 14(5): 3120–3129. doi: 10.1039/D0EE03898A
29. Boruvkova K, Wiener J. Water absorption in carboxymethyl cellulose. *AUTEX Research Journal* 2011; 11(4): 110–113. doi: 10.1002/advs.202103894
30. Zheng W, Gao J, Wei Z, et al. Facile fabrication of self-healing carboxymethyl cellulose hydrogels. *European Polymer Journal* 2015; 72: 514–522. doi: 10.1016/j.eurpolymj.2015.06.013
31. Zhu Y, Xiao S, Li M, et al. Natural macromolecule based carboxymethyl cellulose as a gel polymer electrolyte with adjustable porosity for lithium ion batteries. *Journal of Power Sources* 2015; 288: 368–375. doi: 10.1016/j.jpowsour.2015.04.117
32. Chen M, Chen J, Zhou W, et al. High-performance flexible and self-healable quasi-solid-state zinc-ion hybrid supercapacitor based on borax-crosslinked polyvinyl alcohol/nanocellulose hydrogel electrolyte. *Journal of Materials Chemistry A* 2019; 7(46): 26524–36532. doi: 10.1039/C9TA10944G
33. Li H, Liu Z, Liang G, et al. Waterproof and tailorable elastic rechargeable yarn zinc ion batteries by a cross-linked polyacrylamide electrolyte. *ACS Nano* 2018; 12(4): 3140–3148. doi: 10.1021/acsnano.7b09003
34. Mugheri AQ, Samtio MS, Sangah AA, et al. Promoting highly dispersed Co₃O₄ nanoparticles onto polyethylene unraveling the catalytic mechanism with stable catalytic activity for oxygen evolution reaction: From fundamentals to applications. *International Journal of Hydrogen Energy* 2021; 46(71): 35261–35270. doi: 10.1016/j.ijhydene.2021.08.074
35. Zhou M, Guo S, Li J, et al. Surface-preferred crystal plane for a stable and reversible zinc anode. *Advanced Materials* 2021; 33(21): 2100187. doi: 10.1002/adma.202100187
36. Liu Y, Hu J, Lu Q, et al. Highly enhanced reversibility of a Zn anode by in-situ texturing. *Energy Storage Materials* 2022; 47: 98–104. doi: 10.1016/j.ensm.2022.01.059
37. Zhang B, Qin L, Fang Y, et al. Tuning Zn²⁺ coordination tunnel by hierarchical gel electrolyte for dendrite-free zinc anode. *Science Bulletin* 2022; 67(9): 955–962. doi: 10.1016/j.scib.2022.01.027
38. Yang Q, Li L, Hussain T, et al. Stabilizing interface pH by N-modified graphdiyne for dendrite-free and high-rate aqueous Zn-ion batteries. *Angewandte Chemie International Edition* 2022; 134(6): e202112304. doi: 10.1002/ange.202112304
39. Sun W, Wang F, Hou S, et al. Zn/MnO₂ battery chemistry with H⁺ and Zn²⁺ coinsertion. *Journal of the American Chemical Society* 2017; 139(29): 9775–9778. doi: 10.1021/jacs.7b04471
40. Wang X, Li Y. Selected-control hydrothermal synthesis of α- and β-MnO₂ single crystal nanowires. *Journal of the American Chemical Society* 2002; 124(12): 2880–2881. doi: 10.1021/ja0177105

Appendix

The materials and methods used for the synthesis of cobalt oxide nanostructures using polyethylene polymers are described as follows:

- **Materials**

Polyethylene, hexamethyl tetramethyl amine (HMT), potassium hydroxide, cobalt chloride hexahydrate, and alcohol

- **Synthesis methodology**

Preparation of Equimolar Cobalt Chloride Hexahydrate and HMT Solutions Two individual beakers, each with a volume of 100 mL, were taken. In each beaker, an equimolar solution of cobalt chloride hexahydrate (0.1M) and HMT was prepared. **Addition of Polyethylene to Cobalt Chloride Solution** 20 mg of polyethylene was added directly to one beaker containing the cobalt chloride solution, labeled as Co/polyethylene 20 mg. The solutions in both beakers were continuously stirred on a magnetic stirrer for 20 min to obtain a uniform solution. The homogeneous solutions of pristine (Co/polyethylene, 20 mg) and composite were properly covered with aluminum foil. The growth solutions were kept in an electric oven at 95 °C for 5 h. After the growth period, the solutions were filtered using common filter paper to collect the nanostructures of pristine and composite materials. The collected nanostructures were dried at room temperature. Finally, the dried nanostructures of both pristine and composite materials were annealed at 500 °C for 3 h to obtain the final product.

- **Preparation of the polyethyne electrolyte**

Polyethyne membrane 2M nanocomposite material (for Co plating/stripping tests) and 0.1 M MnSO_4 ($\text{Co}||\text{MnO}_2$ full cell tests in aqueous solution). Take the nanocomposite material and place it in a container for Co plating/stripping tests. For $\text{Co}||\text{MnO}_2$ full cell tests, immerse in an aqueous solution. Let the nanocomposite material soak in the respective solution overnight to allow proper absorption of the electrolyte. Squeeze-drying. After the immersion period, remove the polyethyne membrane from the solution. Ensure the membrane is evenly sandwiched between the Kimwipes. This process will result in the formation of the nanocomposite electrolyte. Once the squeeze-drying is complete, carefully separate the polyethyne membrane. The squeezed membrane is now converted into the nanocomposite electrolyte and is ready for use in Co plating/stripping tests or $\text{Co}||\text{MnO}_2$ full cell tests, depending on the type of immersion solution used. The prepared nanocomposite electrolyte is essential for conducting experiments related to Co plating/stripping or building $\text{Co}||\text{MnO}_2$ full cells. Make sure to handle the electrolyte with care and follow proper safety procedures while conducting any tests.

H₂O Retention Measurements: The H₂O retention measurements described involve evaluating the H₂O absorption capacity and H₂O-holding ability of the membranes. These measurements are crucial in understanding the membrane's characteristics and performance in different environmental conditions. Here's a step-by-step explanation of the procedure. Take the polyethyne membranes and dry them in an oven at 100 °C for 12 h. This step ensures that all the H₂O present in the membranes is removed, leaving them in a completely dry state. After the drying process is complete, remove the membranes from the vacuum oven and let them cool to room temperature in a controlled environment (such as a desiccator) to prevent any moisture absorption before the test. Weigh the dried membranes using a precise balance and record their masses of dry membrane. Submerge the dried membranes in deionized H₂O for 1 h. Ensure that the H₂O completely covers the membranes during this soaking period. After 1 hour, carefully remove the soaked membranes from the H₂O, allowing any excess H₂O to drain off the surface. After determining the H₂O uptake, take the same soaked membranes from the previous test and place them in an environment with a temperature of 25 °C and 1% humidity. This controlled environment ensures minimal H₂O loss due to evaporation during the test. At regular

intervals (e.g., every 20 min), weigh the membranes using the precise balance and record their masses. The weighing process should be performed quickly to minimize exposure to the surrounding atmosphere. Continue recording the masses at the specified time intervals for an appropriate duration (e.g., a few hours) or until a steady state is achieved, indicating that H₂O loss has reached equilibrium. The H₂O uptake measurement provides information about how much H₂O the dry membranes can absorb, while the H₂O retention test helps understand how well the soaked membranes can retain H₂O over time in a low-humidity environment. These measurements are valuable in assessing the suitability of the membranes for various applications, such as fuel cells, batteries, or H₂O purification systems.

- **Electrochemical Impedance Spectroscopy (EIS)**

Electrochemical Impedance Spectroscopy (EIS) tests were performed within a CR2032 coin cell. The nanocomposite electrolyte is between the two stainless steel plates and sealed inside the coin cell to ensure a stable and controlled environment during the EIS measurements. The EIS test parameters included an amplitude of 10 mV and an open-circuit voltage condition. The 10-mV amplitude represents the perturbation voltage applied during the EIS measurements. An open-circuit voltage means that the cell is not subjected to any external current flow during the measurements. The EIS technique provides valuable information about the electrochemical properties of the composite electrolyte, including its ionic conductivity, charge transfer resistance, and capacitance. By varying the frequency of the applied perturbation voltage, EIS generates a complex impedance spectrum, which can be analyzed to gain insights into the electrochemical behavior of the system.

- **Transference number measurement**

To measure the Co²⁺ transference number using the Bruce-Vincent method, Co||Co cells were used for the transference number measurements. This means that the Co metal was used as both the working electrode and the counter/reference electrode. The electrolyte used in the cell contained Co²⁺ ions. A DC polarization measurement was conducted in the Co||Co cell, and a difference of $\Delta V = 10$ mV was applied across the cell to create an electric field. This steady-state condition is crucial for accurate measurements. By comparing the EIS data before and after DC polarization, changes in impedance can be observed. These changes are associated with the migration of specific ions (in this case, Co²⁺ ions) within the electrolyte. The transference number provides information about the fraction of the total current carried by Co²⁺ ions in the electrolyte during the electrochemical process. The measurement of transference numbers is essential in understanding the transport behavior of ions in the electrolyte, which is critical for optimizing the performance and efficiency of electrochemical systems, such as batteries and fuel cells. The Bruce-Vincent method is a widely used technique for determining transference numbers and is particularly suitable for systems where ion transport plays a significant role.

- **Co plating/stripping for the electrochemical tests**

Co cells remained accumulated for the Co foils for the anode and cathode, and either the aqueous media electrolyte (120 μ L 2 m composite material) or the or the addition of glass fiber. The Cu||Co cells are combined with Co foil for the purpose of anode and cathode. Galvanostatic stripping was employed and measured. The information provided describes the setup and testing conditions for assembling and testing Co-symmetric cells and asymmetric Cu||Co cells. These cells are used to study the galvanostatic plating/stripping behavior of zinc in different electrolyte configurations. Here's a breakdown of the key components and procedures involved: This is a non-aqueous electrolyte containing the polyethylene membrane, which acts as a separator and allows for ion conduction. A glass fiber separator is used to separate the cathode and anode in the Co symmetric cells. The setup described allows researchers to investigate and compare the galvanostatic plating and stripping behavior of Co in different electrolyte configurations and in asymmetric cell setups with Cu as the cathode. These experiments are valuable for studying the electrochemical performance and behavior of cobalt-based

systems and can help in the development and optimization of various electrochemical energy storage devices and battery technologies.

- **Electrochemical tests for Co||MnO₂ full cell**

The synthesis and preparation of MnO₂ nanorods and composite electrodes for electrochemical testing. The evaluation of the electrochemical performance is conducted using coin cells with a Co foil anode and composite material as an electrolyte, and the testing is carried out at room temperature. MnO₂ nanorods are synthesized as reported in the literature reference^[40].