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Carbonized Polymer Dots as Electrolyte Additives to Inhibit Zinc Anode Corrosion and Enhance Full Cell Cycle Life

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Abstract

Carbonized polymer dots(CPDs), as a new type of carbon-based nanomaterials, have been widely used in the fields of biosensing[1], light-emitting devices[2], and energy storage systems[3-4]due to their tunable photovoltaic properties and abundant surface functional groups. Especially in energy storage, it has good prospects and applications as an artificial negative electrode protective layer[5] for zinc-ion batteries(AZIBs). However, less research has been done on its use as an additive in zinc ion battery electrolyte[6]. We developed a method for the rapid synthesis of CPDs using citric acid as a substrate and urea as a nitrogen-doped additive using the microwave method at 1000W. The synthesized CPDs have graphitized carbon core centers as well as a wide range of peripheral functional groups. Due to the great potential of CPDs in the field of zinc ion batteries, we applied them as electrolyte additives in the electrolyte of aqueous zinc ion batteries, which can effectively inhibit the growth of dendrites on zinc anode, the precipitation of hydrogen and oxygen in the electrolyte, and at the same time, the corrosion current of the electrolyte on the anode is extremely low, which can greatly inhibit the corrosion of zinc anode in the electrolyte, and can effectively promote the rapid diffusion of zinc ions from the two-dimensional to the three-dimensional, which can greatly improve the long-cycle stability of zinc ion battery, as well as the stability of the long-cycle stability of the zinc ion battery. It can also effectively promote the rapid diffusion of zinc ions from two-dimensional to three-dimensional, which greatly improves the long cycle stability of zinc ion battery and the cycle life of the whole battery. The zinc iodine battery has a stable cycle time of 43,000 cycles, a capacity retention rate of 90%, and a Coulombic efficiency of 100%.

Keywords: *CPDs; microwave method; dendrite growth; corrosion; cyclic stability*

1 Introduction

In recent years, with the transition of global energy structure to renewable energy, large-scale energy storage technology has become the key to solve the stability of intermittent energy sources. However, the current mainstream lithium-ion batteries have hindered their marketability in the energy storage industry due to potential problems such as high cost, resource depletion and flammability of organic electrolyte[7-8]. Therefore, the development of secondary batteries with the advantages of safety, high efficiency, environmental protection and low cost has gradually become a trend[9]. The aqueous zinc ion battery has become a highly promising energy storage device due to its unique advantages. Zinc ion adopts non-flammable aqueous electrolyte, which fundamentally solves the risk of thermal runaway; zinc resources are abundant and inexpensive, which significantly reduces the cost of raw materials; at the same time, zinc is non-toxic, easy to recycle, and has better environmental compatibility. In addition, zinc anode has high theoretical specific capacity (820 mAh g^{-1}) and low electrochemical potential (-0.76 V)[10], with manganese-based, vanadium-based anode materials can realize efficient energy storage and fast charge and discharge. However, at the same time, zinc ion batteries also face certain problems, for example, the surface of zinc negative electrode is prone to tip effect due to the uneven distribution of electric field, forming dendritic crystal growth, piercing the diaphragm and causing short circuit, and hydrogen precipitation and chemical corrosion inevitably occurs in the aqueous electrolyte, which greatly reduces the cycling stability and coulombic efficiency of zinc ion batteries[11]. Therefore, based on the defects of zinc ion batteries, the use of microwave method to prepare citric acid, urea carbon point, as an electrolyte additive, not only can effectively inhibit the zinc negative electrode dendrite growth, electrolyte hydrogen precipitation and oxygen precipitation reaction, but also can improve the transmission efficiency of Zn^{2+}, and greatly improve the zinc ion batteries long-cycle stability, and the performance of the whole battery.

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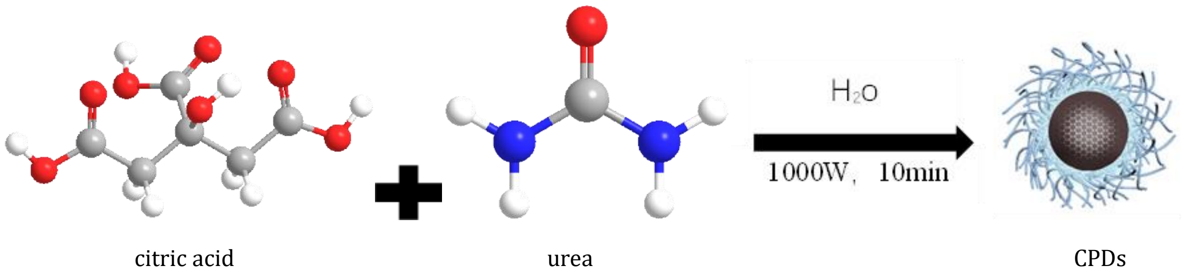

Figure 1 Synthesis of CPDs

2 Synthesis Method

As shown in Figure 1, the carbonized polymer dots were successfully synthesized by microwave method using citric acid and urea as substrates and water as solvent, and reacted for ten minutes at 1000 W. This synthesis method is low cost, easy to prepare, and the quantum yield of the reaction is high, while having good water solubility.

3 Experimental Part

3.1 Electrochemical test properties

The synthesized carbon dots were added to the 2M $ZnSO_4$ electrolyte at 3 mg / mL and stirred overnight at room temperature. The prepared electrode solution was added to the button cell for testing. Tafel and hydrogen evolution reaction tests allowed comparison of the corrosion behavior of the zinc negative electrode in the two electrolytes before and after the addition of CPDs. As shown in Figure 2 (a), the corrosion current of zinc negative electrode in $ZnSO_4$ electrolyte with CPDs added decreased from 1.156 mA cm^{-2} to 0.1257 mA cm^{-2}, which indicates that the zinc negative electrode is well protected by the addition of CPDs, and there is almost no by-products such as zinc alkali sulfate generated, which can effectively inhibit the occurrence of corrosion reaction. From the hydrogen precipitation curve in Figure 2 (b), it can be seen that the zinc negative electrode has a more negative potential response in the electrolyte containing CPDs at the same current density. It proves that CPDs contain more strongly paired functional groups with lone pair of electrons, which are able to pair with zinc ions, making the existence of free and structured water around zinc ions in the electrolyte change in form, and better inhibiting the reduction of hydrogen ions. As shown in the oxygen uptake curve in Figure 2 (c), the electrochemical stabilization window of the electrolyte with added CPDs increased from 2.52 V to 2.56 V, indicating that CPDs can be adsorbed on the electrode surface to occupy the active sites of oxygen molecules, hindering the adsorption and reduction of oxygen and inhibiting the oxygen-induced corrosion reaction. At the same time, by CA curves of zinc ion batteries under two different electrolytes, it can be concluded that the 2D to 3D diffusion transition after adding CPDs appears faster or slower, as in Figure 2 (d), the 2D to 3D transition of the $ZnSO_4$ electrolyte is in 100 s, while the 2D diffusion to 3D diffusion transition of the electrolyte with the addition of CPDs has already occurred in only 27 s, and the quicker transition it can effectively improve the ion transport efficiency and electrode kinetic performance, enhance the utilization of active sites, and alleviate the dendrite growth problem.

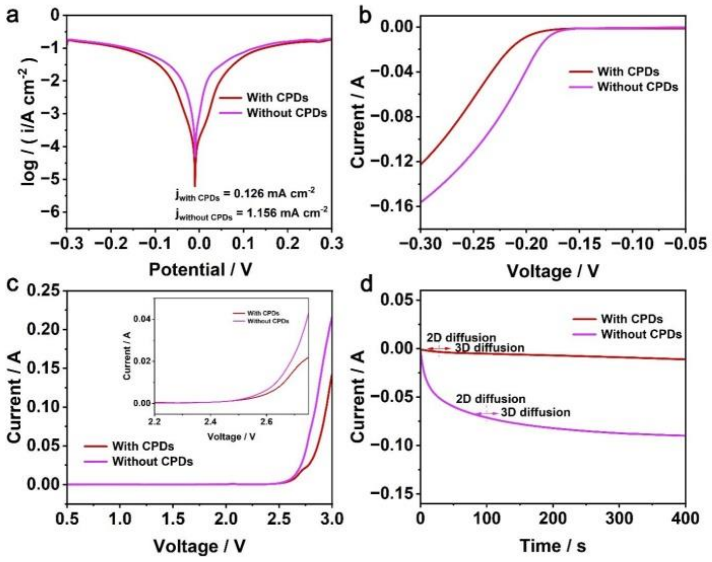

Figure 2 (a) Tafel curves. (b) HER test. (c) LSV curves. (d) Chronoamperometry (CA) curves for zinc negative electrode

Next, the electrochemical impedance (EIS) test was performed on the cell, and it can be concluded from Figure 3 (e) that the charge transfer resistance of the cell in the electrolyte containing CPDs is significantly lower than that in the $ZnSO_4$ electrolyte without CPDs, indicating that there is a fast ion transfer capability within it, so that the zinc ions and the electrons can have a fast reaction at the solid-liquid interface to alleviate the zinc deposition and improve the electrochemical performance. The values of ionic conductivity as well as ion mobility number were measured to demonstrate that the addition of CPDs has improved the ion transport kinetics of zinc ions. As shown in Figure 3 (f), the ionic conductivity of the cell was tested using electrochemical impedance test, and it was calculated that the ionic conductivity of the electrolyte with the addition of CPDs was 29.9 mS cm^{-1}, while the ionic conductivity of the electrolyte without the addition of CPDs was 24.2 mS cm^{-1}, which is a more obvious difference, indicating that the addition of CPDs effectively improves the ion transport kinetics. As shown in Figure 3 (g, h), the timed current method combined with electrochemical impedance method was utilized to indicate the transference ability of zinc ions under different electrolytes. It can be calculated that the ion mobility number in the electrolyte containing CPDs is 0.44, while the ion mobility number in the electrolyte without CPDs is only 0.17, which is because CPDs have abundant functional groups on the surface that can be combined with zinc ions, have a conductive effect to promote the transport of zinc ions, and guide the homogeneous deposition of zinc ions to inhibit the growth of branching crystals, which can effectively improve the ion transport kinetics.

3.2 Cell properties

In order to test the effect of CPDs on the electrochemical properties, we assembled Zn||Zn symmetric cells for cycle profile determination. As shown in Figure 4 (a), at a current density of 2 mA cm^{-2} and a capacity of 1 mAh cm^{-2}, the Zn||Zn symmetric cell under the $ZnSO_4$ electrolyte without CPDs completely short circuit after only 80 h of cycling, whereas the Zn||Zn symmetric cell under the electrolyte containing CPDs was able to cycle stably for more than 873 h, with a cycling life of about eleven times longer than that of the former. Moreover, as shown in Figure 4 (b) shows the enlarged cycling curves of the battery under the two electrolytes for the first 10 h. It can be seen that the polarization voltage of the battery is smaller after adding CPDs, which makes it easier for the zinc ions to nucleate uniformly, and effectively reduces the charge transfer impedance and interfacial resistance inside the battery, and promotes the rapid and uniform transmission of zinc ions. Figure 4 (c), the voltage of the former can still be kept very stable in the last 10 h of the cycle, and this gap strongly proves that the CPDs have high electrical conductivity and rich surface functional groups, which not only promote the uniform deposition of zinc ions and inhibit the growth of dendritic crystals, but also regulate the ionic flow through the distribution of the surface charge, reduce the side reactions and electrode corrosion, and effectively solve the common problems of zinc batteries, such as poor reversibility and short life.

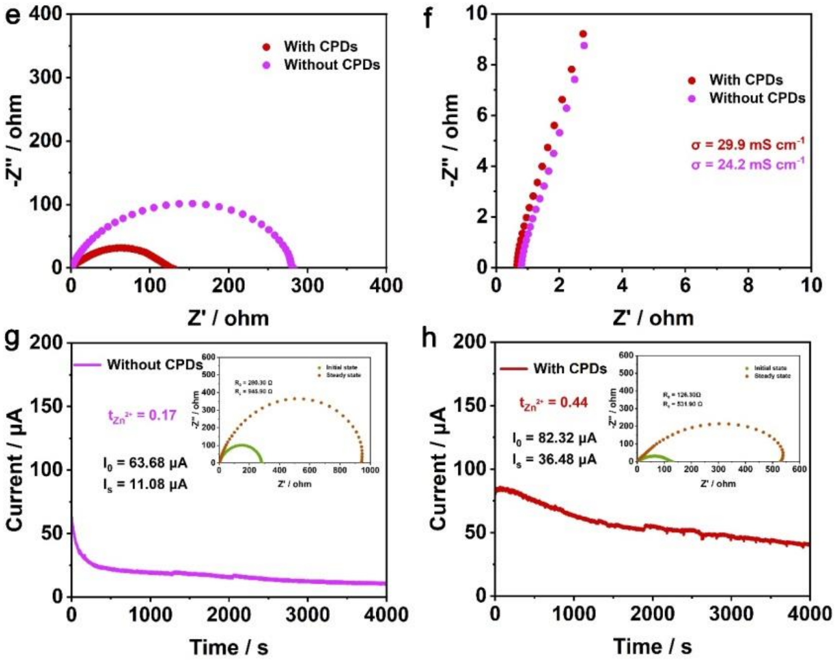

Figure 3 (e) EIS test for symmetric cell. (f) Ionic conductivity of both electrolytes. (g, h) Ionic transference number of both electrolytes

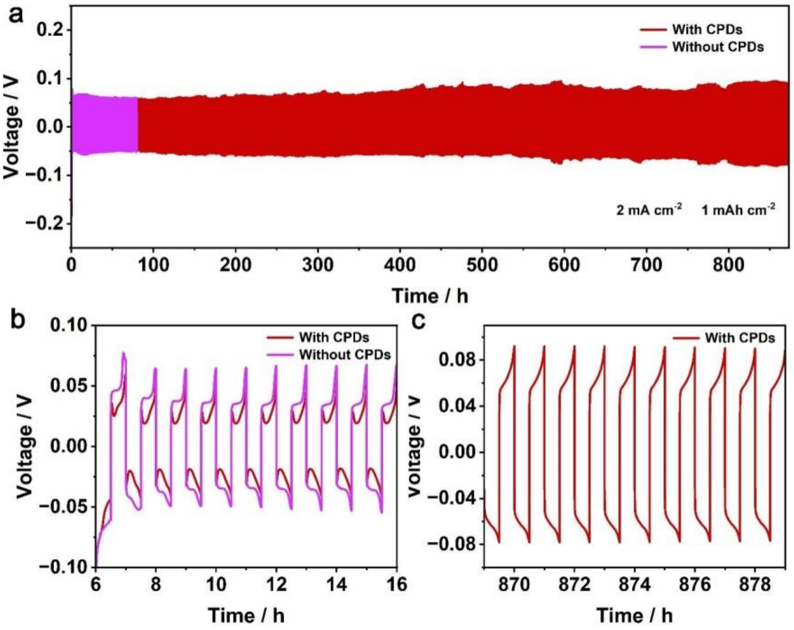

Figure 4 (a) Cycling properties of Zn||Zn symmetric cell at 2 mA cm^{-2} 1 mAh cm^{-2} current density. (b) Cycling magnification of the first 10 h. (c) Cycling magnification of the second 10 h

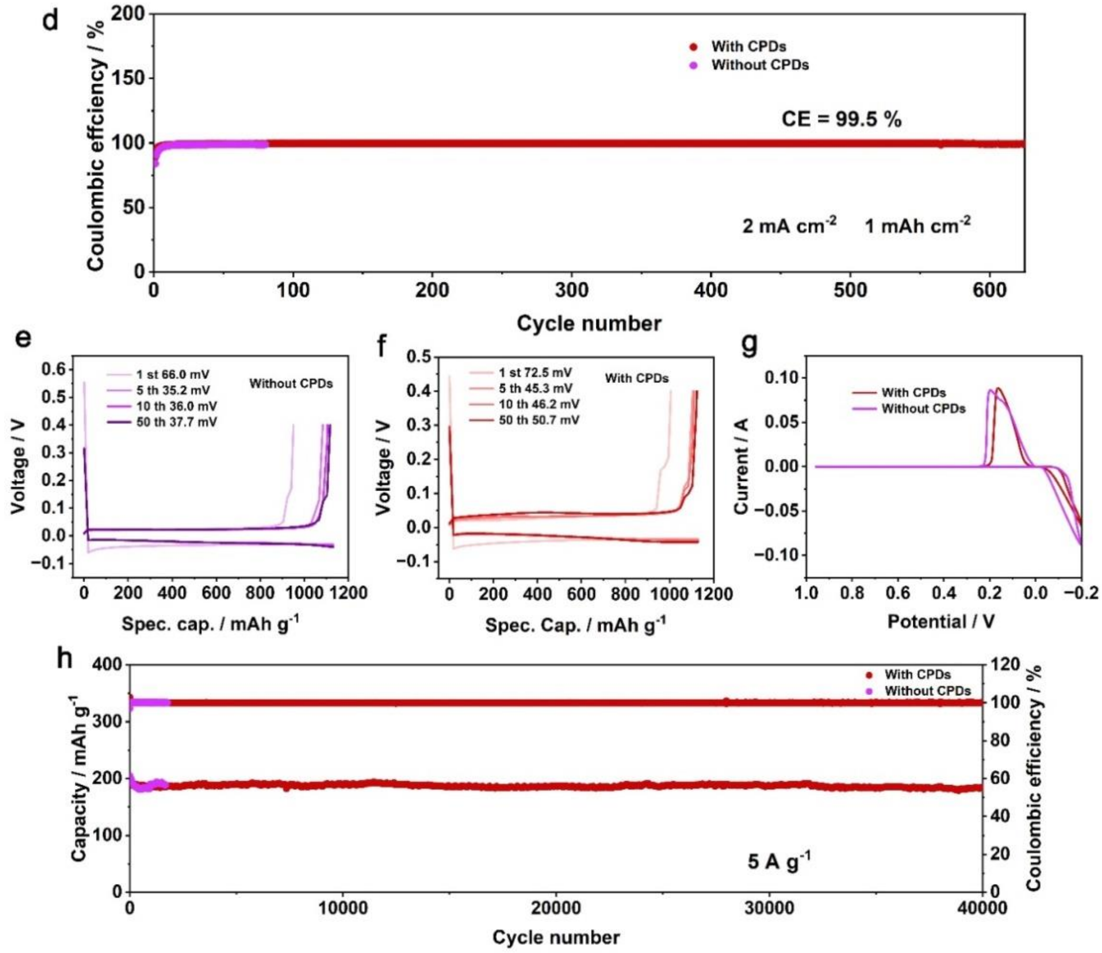

Figure 5 (d) Coulombic efficiency at 2 mA cm^{-2} 1 mAh cm^{-2} current density. (e, f) Capacity-voltage curves for different number of turns. (g) CV curves. (h) Cycling performance of the Zn || I_2 full cell at 5A g^{-1}

In addition to the stable cycling performance, CPDs as electrolyte additives can also exhibit excellent Coulombic performance in Zn||Cu asymmetric batteries. As shown in Figure 5 (d), under the condition of current density of 2 mA cm^{-2} and capacity of 1 mAh cm^{-2}, the Coulombic efficiency is unstable and the battery is short-circuited after cycling for 80 cycles in the battery with only $ZnSO_4$ electrolyte, whereas the electrolyte containing CPDs is still stable after cycling for 626 cycles and is able to reach more than 99.5%, which indicates that the CPDs are able to optimize the zinc ions' deposition/dissolution behavior, inhibit the growth of dendrites, and prevent piercing the diaphragm leading to battery short circuit.

In order to verify whether CPDs can be used as electrolyte additives for zinc ion batteries to improve the cycling performance of the batteries in practical applications. We assembled a Zn||I_2 full battery with I_2 as the cathode material. As shown in Figure 5 (h), the cell with CPDs added was able to cycle stably for about 43,000 cycles at a discharge specific capacity of about 190 mAh g^{-1} under 5 A g^{-1}, with a capacity retention of up to 90%, and the Coulombic efficiency could be maintained at 100% at all times. In contrast, the cell without CPDs electrolyte completely deteriorated after only 670 cycles, and the cycle life was drastically reduced. It is proved that the addition of CPDs can not only inhibit the dendrite growth and corrosion reaction of zinc ions, but also anchor the free iodine species by the rich oxygen/nitrogen-containing functional groups on the surface of CPDs, inhibit the shuttle effect of multiple iodides, and minimize the loss of active substances, which greatly improves the cycling stability and the Coulombic performance of the battery.

As shown in Figure 5 (e, f), the capacity voltage curves of the two electrolytes added to the cell at different number of laps, the addition of CPDs may be due to the introduction of a large number of electrolyte additives resulting in a slight increase in polarization voltage compared to the addition of the $ZnSO_4$ electrolyte, but it does not affect the cycling stability because the polarization voltage is decreasing with the increase of the number of laps. Meanwhile, as shown in Figure 5 (g) in comparing the CV curves of the two, it can also be found that the nucleation overpotential of the asymmetric cell decreases after the addition of CPDs, and the energy barrier decreases, which is conducive to the generation of zinc monomers by the reduction of zinc ions.

4 Conclusions

In summery, in order to solve the problem of zinc ion batteries hindering their development in large-scale energy storage systems due to the defects of dendrite growth, corrosion and hydrogen precipitation reaction, the electrolyte of zinc ion batteries is modified by adding carbonized polymer dots (CPDs), which are rapidly synthesized by microwave method using citric acid and urea as the substrate, as the additive of electrolyte. Through a series of electrochemical tests, cycling and coulometric performance tests, we found that CPDs have a strong adsorption capacity for Zn^{2+}, which can not only change the solvation structure of Zn^{2+}, inhibit corrosion, and reduce the occurrence of side reactions, but also improve the transport rate of Zn^{2+}, induce uniform deposition of zinc ions, and inhibit the growth of zinc ions dendritic crystals, Thus improving the properties of zinc-ion batteries. Ultimately providing a referenceable method for the development of zinc ion batteries.

Data availability: The data that support the findings of this study are available within the paper.

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