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Efficient mass transfer in electrodes is essential for the electrochemical processes of battery charge and discharge, especially at high rates and capacities. This study introduces a 3D electrode design featuring layered double hydroxides (LDHs) nanosheets array grown in situ on a carbon felt surface for flow batteries. The mesoporous structure and surface characteristic of LDH nanosheets, especially, the hydroxyl groups forming a unique "H-bonding-like" geometry with ferrous cyanide ions, facilitate efficient adsorption and ion transport. Thus, the designed LDHs electrode enables the alkaline zinc-iron flow battery to maintain a voltage efficiency of 81.6% at an ultra-high current density of 320 mA cm⁻², surpassing the values reported in previous studies. The energy efficiency remains above 84% after 375 cycles at a current density of 240 mA cm⁻². Molecular dynamics simulations verify the enhanced adsorption effect of LDH materials on active ions, thus facilitating ion transport in the battery. This study provides a novel approach to improve mass transport in electrodes for alkaline flow batteries and other energy storage devices.

1. Introduction

With the escalating energy crisis, the need for energy storage and the utilization of renewables has become increasingly evident. However, the intermittency and variability of renewable energy have made large-scale energy storage, especially redox flow batteries, a key technology for addressing practical application issues.^[1–3] Researchers have explored a wide

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array of redox couples to enhance the cycling stability and efficiencies of flow cells. Among various redox flow batteries, alkaline zinc-iron flow battery (AZ-IFB) system utilizes cost-effective ferrocyanide/ferricyanide as the positive redox couple and zincate/zinc (-1.22 V vs standard hydrogen electrode [SHE]) as the negative redox couple. This configuration enables the battery to achieve a high voltage of up to 1.81 V in high-concentration electrolytes.^[4] Studies have indicated the development of a kilowatt-scale reactor costing less than \$11 kWh⁻¹,^[5,6] demonstrating the cost-effectiveness of the system. Nevertheless, the energy storage cost and footprint of the AZIFB have remained high due to its low current density.^[7]

The high concentration polarization loss observed on the positive side is a key obstacle to achieving a high current density.^[8] Enhancing ion transfer at the interface is essential to improve battery performance.^[9]

Due to the rapid reaction kinetics of the ferrocyanide/ferrocyanide couple^[10,11] and the low solubility of the ferrous cyanide ion itself,^[12] (note: its solubility was reported to be 0.4 mol L⁻¹ in alkaline electrolytes.^[13]) concentration polarization plays a major role in all polarization losses, especially at a high current density. Although plenty of previous studies have focused on the advancement of anode materials and electrolytes, the role of the ferrocyanide/ferrocyanide couple (0.360 V vs

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SHE) at the cathode surface warrants increased attention, given its high stability and kinetics^[14] but relatively low ion transfer rate.^[15]

Therefore, improving the mass transfer ability of the active material in the positive electrode is essential for breaking through the critical current density limitation. Researchers have developed various methods to improve the mass transfer rate of active materials at the electrode surface, including enhancing interface wettability,^[16] increasing local charge density,^[17] optimizing pore structure,^[18] etc.^[19] The introduction of mesoporous structures (2-50 nm) on the electrode surface is an efficient way to enhance mass transfer.^[20] Both the etching of mesopores on the surface of the material^[21,22] and the introduction of other mesoporous materials^[23] could significantly improve the electrochemical properties of the material. Many studies have shown that the mesopores on the carbon fiber surface can increase the specific surface area of the electrode and shorten the ion diffusion distance to enhance the diffusion capacity.^[24] Moreover, the addition of mesopores can disrupt the flow of the electrolyte, leading to increased turbulence and local flow velocity of the electrolyte fluid.^[25] Currently, the technique for enhancing mass transfer via mesoporous structures is extensively applied in various types of electrochemical materials, such as all-vanadium flow batteries,^[26] supercapacitors,^[27] zinc-ion batteries,^[28] etc.

An alternative approach involves leveraging the transport properties of materials to facilitate the movement of different substances. Layered double hydroxides (LDHs) are promising materials that possess the ability to enhance ion transport. LDHs are a type of 2D anionic clay with a uniform interlayer structure. Their chemical formula is $[M_{1-x}^{2+}, M_x^{3+}(OH)_2]^{x+}A_{x/n}^{n-}zH_2O$, where M²⁺ and M³⁺ denote di- and trivalent metal ions, respectively, Aⁿ⁻ represents n-valent anions, and H₂O represents the interlayer water. The positively charged nature, abundant hydroxyl groups on the surfaces of partially LDHs, and interlayer channels allow anions^[29] or water molecules to enter or leave, significantly enhancing ion transport.^[30] However, the transport behavior of ions through LDHs and their applications in energy storage have rarely been investigated. Recently, a study exploring ion transport behaviors in alkaline environments revealed that LDHs could facilitate the rapid conduction of hydroxide ions through the Grotthuss mechanism.^[31] Therefore, innovative approaches such as the in situ growth of an array of LDHs as a functional layer on carbon felt presents a promising avenue for enhancing mass transfer and addressing the problem of concentration polarization associated with alkaline flow batteries.

The current research has mainly focused on either the structural properties of mesopores or ion transport mechanisms in different materials. Few studies have considered both of these factors. In fact, at the nanoscale, the adsorption process occurring between the material surface and the molecule exerts a substantial effect on the mass transfer rate in mesopores.^[23] Integrating mesoporous structural design with material adsorption characteristics can considerably enhance ion transport.

Herein, we first propose a novel strategy to enhance mass transfer in the AZIFB system through the in situ growth of MgAl-LDH nanosheets on the surface of carbon felt (referred to as LDH-CF) as the positive electrode (**Figure 1**). The engineered LDH-CF, enriched with a substantial mesoporous framework, significantly enhanced the mass transfer of positive active ions on the electrode surface. Moreover, abundant hydroxyl groups dispersed throughout LDHs sheets facilitate therapid transport of active ions, effectively mitigating concentration polarization of flow batteries. Molecular dynamics (MD) simulations verified the unique "H-bonding-like" geometry between hydroxyl groups on the mesoporous surface and ferrous cyanide ions. This strategy led to improvements in the voltage efficiency (VE) and energy efficiency (EE) of AZIFBs, resulting in excellent performance even at extremely high current densities. Even at a high current density up to 320 mA cm⁻², the EE could be maintained at 80%, which is the highest performance reported so far. The high mass transfer rate of LDH-CF is beneficial for reducing concentration polarization in AZIFBs, enabling the efficient operation of flow batteries at high-current densities. The proposed electrode modification strategy can also be extended to other alkaline flow batteries.

2. Results and Discussion

Growing LDHs structures directly on the electrode surface in situ poses a substantial challenge. The low electrical conductivity of LDHs materials and complete coverage of the electrode surface by LDHs would introduce additional interfacial resistance detrimental to charge transfer. As shown in **Figure 2**a, carbon felt was used as a substrate. LDHs nanosheets were grown in situ on the surface of the carbon fiber to enhance the mass transfer rate of active ions within the diffusion layer (Figure S1, Supporting Information). LDHs array structure grew vertically on the surface of the carbon fiber, and the nanosheets interlocked to form interconnected porous structures. By carefully adjusting the parameters of the hydrothermal treatment process, we controlled the morphology of LDHs grown on the carbon fiber surface to promote growth in a perpendicular plate-like form, ensuring that LDHs did not completely cover the electrode surface.

To examine morphological changes in the carbon fiber surface following the introduction of LDHs, we performed scanning electron microscopy (SEM) to observe the LDH-CF surface structure. Figure 2b shows the original morphology of the carbon felt used as the substrate. The fiber surface was relatively clean and free of impurities. After hydrothermal treatment, the carbon fiber surface was enveloped by a layer of hexagonal platelike LDHs nanosheets (Figure 2c-e; Figure S1, Supporting Information). These nanosheets were densely and uniformly distributed across the carbon fiber surface, intersecting at various points. Furthermore, transmission electron microscopy (TEM) images (Figure 2f; Figure S2, Supporting Information) provided insights into the shape and size of LDHs nanosheets. They exhibited a hexagonal plate-like shape with neat edges and no fractures, with each side measuring \approx 300 nm. Atomic force microscopy (AFM) was used to capture the real morphology of LDH-CF. As revealed by Figure 2g, the surface of LDH-CF exhibited protrusions with a height of ≈ 200 nm, aligning with the dimensions of LDH nanosheets observed in TEM images. Energy-dispersive X-ray spectroscopy (EDS) confirmed the successful growth of hexagonal nanosheets on the carbon fiber surface (Figure 2h) and the presence of magnesium (Mg), aluminum (Al), and oxygen (O) elements in their composition. The atomic ratio of Mg to Al was \approx 2:1, which was consistent with the concentration of the solution used (Figure 2i).





Figure 1. Schematic illustration of ion transfer in the surface of LDH-CF.

In the positive electrode of AZIFBs, active ions $(Fe(CN)_6^{4-}/$ $Fe(CN)_{6}^{3-}$ in the electrolyte penetrate into the carbon felt and then reach the carbon fiber surface through diffusion to undergo oxidation-reduction reactions before leaving. Based on the designed structures, the introduction of mesopores through enclosing LDHs nanosheets was expected to enhance the diffusion of active ions on the electrode surface. Mesopores could shorten the diffusion distance of ions on the electrode surface and increase the local flow rate of the electrolyte fluid, facilitating the rapid transfer of ions. To characterize the newly introduced pores, the pore size distribution, physical specific surface area, and electrochemical specific surface area (ECSA) of the samples were measured. The N₂ gas adsorption-desorption isotherms of pristine carbon felt and LDH-CF (Figure 3a) belonged to type IV adsorption isotherms. The samples exhibited a significant hysteresis loop in adsorption and desorption processes, indicative of, which presented mesoporous structures contributed by the LDHs nanosheets array. Figure 3b shows the nanoscale pore size distribution of the samples measured using the Brunauer-Emmett-Teller (BET) method. The exact pore size and distribution of mesopores are illustrated in Figure 3b. As seen, LDH-

CF had nearly twice as many mesopores as CF. The pore size of these added pores was $\approx 2-3$ nm, which confirmed that the introduction of the LDHs nanosheets structure brought more mesoporous structures. The vertically distributed LDHs nanosheets also increased the electrode's specific surface area, as demonstrated by the physical specific surface area data measured using the BET method. The specific surface areas of LDH-CF and CF were 3.56 and 8.28 m² g^{-1} , respectively. The larger pores between fibers were measured using the mercury intrusion porosimetry (MIP) method. Figure 3c shows the distribution of large pores measured by MIP. Compared with the original CF, the peak of the pore size distribution curve of LDH-CF remained unchanged, but the peak position shifted to the left. This finding indicated a reduction in the size of large pores in LDH-CF (from 120 to 80 µm). This can be attributed to the increase in the diameter of fibers caused by the growth of LDHs nanosheets on the carbon fiber surface, which led to a decrease in the diameter of the gaps between fibers while keeping their number unchanged.

Under normal operating conditions, the electrolytes may not reach all areas of the surface of the electrode. To obtain a more precise understanding of the variation in the accessible surface ADVANCED SCIENCE NEWS ______



Figure 2. a) Schematic illustration of LDH-CF preparation process. b) SEM image of pristine carbon felt. c–e) SEM images of LDH-CF. f) TEM image of LDH. g) AFM 3D surface morphology of LDH-CF. h) Corresponding elemental mappings of LDH-CF. i) EDS diagram of LDH-CF.

area of the electrode surface by the electrolyte, ECSA was measured using cyclic voltammetry. Figure 3d,e depict the cyclic voltammetry curves of CF and LDH-CF at different scan rates, respectively. The scan potential was set between 0 and 0.1 V, avoiding any redox reactions and ensuring that no Faradaic current was generated. The double-layer capacitance value, which represents the ECSA of the electrode, was calculated through the non-Faradaic current. We selected differing current values at the same potential (0.1 V vs SHE) and determined the relationship between the current and scan rate (Figure 3f). The slope of this relationship, obtained using the least squares method for fitting results, represented the capacitance value of the tested sample and the ECSA. The slope of LDH-CF was nearly twice that of CF (0.00791 for LDH-CF and 0.00389 for CF), indicating that the ECSA of LDH-CF was double that of CF. This result was consistent with the specific surface area results obtained by BET.

As indicated by the X-ray diffractometer (XRD) results of the sample (Figure 3g), the peaks of LDH-CF matched well with those of the standard PDF card of $Mg_4Al_2(OH)_{14}$ ·3H₂O (PDF#35-0964). The X-ray photoelectron spectroscopy (XPS) and Fourier infrared spectroscopy (FTIR) test results also confirmed the successful in situ growth of MgAl-LDH on carbon fiber surface.

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Figure 3. a) CO_2 adsorption/desorption isotherms, b) pore size distribution curve measured by BET, and c) pore size distribution curve measured by MIP of pristine CF and LDH-CF. Cyclic voltammetry curves at different scan rates of d) CF and e) LDH-CF. f) Plot of the current versus scan rate at 0.1 V. g) XRD patterns of CF, LDHs, and LDH-CF. h) XPS survey and i) FTIR spectrums of CF and LDH-CF.

Compared with the XPS spectrum of CF, the XPS spectrum of LDH-CF showed peaks indicative of Mg, and Al elements and a higher O peak (Figure 3h; Figure S3, Supporting Information). The higher O peak resulted from the introduction of numerous O atoms and hydroxyl groups in the MgAl-LDH into the sample. The FTIR results exhibited unique characteristic vibration bands on LDH-CF (Figure 3i), consistent with the reported vibrational bands of LDHs. The peaks at 547 and 680 cm⁻¹ were attributed to the lattice vibrations of M-O and M-O-M in LDHs.^[29,32,33] These findings provided strong evidence for the structural characterization of LDH-CF, confirming the presence of MgAl-LDH in the sample.

To investigate the effects of LDH-CF on the mass transfer of active ions, we performed electrochemical impedance spectroscopy (EIS) using a three-electrode testing system to characterize the mass transfer ability of active ions on the electrode surface. As demonstrated in Figure 4a, LDH-CF had a steeper slope in the low-frequency region, indicating lower ion diffusion impedance and confirming the promotion of mass transfer by LDHs. Conversely, in the high-frequency region, the semicircle diameter of LDH-CF was larger than that of CF, implying a greater charge transfer resistance, R_{ct} , and thus a smaller reaction rate constant. This is primarily due to the poor electron conductivity of the LDHs material itself. CV results also supported this conclusion (Figure S4, Supporting Information). LDH-CF showed a higher peak separation ΔE_n , indicating its poor reactivity toward ferrocyanide/ferricyanide. However, this decrease in the reaction rate constant did not affect the performance of LDH-CF as an electrode. As shown in Figure 4b, LDH-CF significantly improved battery performance, primarily due to enhancement of the ion mass transfer process, a critical rate-limiting step in the reaction. The limiting current method was used to quantify the difference in mass transfer performance between the two electrode materials. The mass transfer coefficient $k_{\rm m}$ was multiplied by the

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Figure 4. a) Nyquist diagram of CF and LDH-CF. b) Polarization curves of AZIFB with LDH-CF and CF, respectively. c) ak_m of LDH-CF and CF. Contact angle of d) LDH-CF and e) CF. f) Zeta potential of LDH and CF powders.

specific surface area per unit volume "a" to adjust for the difference in the specific surface area between the two materials. Their limiting currents were obtained according to the polarization curves of the two materials measured at 50% *SoC* (Figure 4b). The modified mass transfer coefficient ak_m was calculated using' Fick's law. The results showed that the modified mass transfer coefficient of LDH-CF was 31.9% higher than that of CF (Figure 4c).

The enhancement in mass transfer is attributed not only to the increased number of mesopores but also to the surface characteristics of LDH materials. The contact angle results are shown in Figure 4d,e. Accurately measuring the contact angle was challenging because the positive electrolyte solution was rapidly absorbed owing to the excellent hydrophilicity of carbon felt. Therefore, the difference in hydrophilicity was determined by analyzing frame-by-frame videos of the liquid absorption process (Figure S5, Supporting Information). It was evident that LDH-CF had a smaller contact angle of 13.4° at 160 ms, indicating that the introduction of LDHs enhanced the hydrophilicity of CF, possibly due to the abundant hydroxyl groups on the surface of the LDHs. The enhanced hydrophilicity made the electrolyte fully wet the electrode surface, facilitating the rapid arrival of active ions at the electrode surface. Moreover, the LDHs layer on platelets was positively charged, resulting in a stronger adsorption capacity for ferrocyanide anions. Zeta potential measurements indicated that LDHs had more positive charge than CF surface. The value of zeta potential for LDH-CF and CF was 29.7 and 12.2 mV, respectively (Figure 4f). Under the combined effects of surface adsorption and mesopores for LDH-CF, the mass transfer rate of ferrocyanide ions on the carbon fiber surface had been improved. This effect is expected to enhance the overall performance of AZIFBs.

To further elucidate the advantages of the LDHs electrode with respect to the sorption of active ions (Fe(CN)₆^{4–}), we performed

a comparative study between LDH and carbon felt electrodes using MD simulations^[34,35] as shown in Figure 5 and Figure S6 (Supporting Information). The carbon fiber surface was simplified to a single layer of graphene (GRA). The number density (ρ_n) of nitrogen atoms in Fe(CN)₆⁴⁻ presented two peaks in areas 0.5 nm away from the LDHs electrode. However, there was negligible ρ_n distribution in a similar region near the GRA electrode (Figure 5b). As shown in the local enlarged drawing of Figure 5a, a unique "H-bonding-like" geometry appeared on the binding site between the LDHs surface and Fe(CN)₆⁴⁻ ions. This type of close interaction was not observed near the GRA surface (Figures S6b and S7, Supporting Information). The H-bonding verified the interaction between the LDH-CF and the Fe(CN)₆⁴⁻. The same results were visible in the analysis for the radial distribution function of LDH-Fe(CN)₆⁴⁻ and GRA-Fe(CN)₆⁴⁻ (Figure S8, Supporting Information). In addition, the van der Waals radius of the hydrogen atom was 0.05 nm shorter than that of the carbon atom. It is expected to positively affect shortening interatomic distance at the solid-liquid interface.^[36]

Further, by investigating the free energy as a function of distance to the electrode surface, we concentrated on the cause of how the electrode influences $Fe(CN)_6^{4-}$ ions. By the umbrella sampling approach, we calculated the potential of mean force (PMF).^[37,38] It represented the variation in free energy with changing the position of one $Fe(CN)_6^{4-}$ ion from the electrode surface toward the bulk electrolyte region.^[39,40] The distance in Figure 5c was calculated from the electrode surface to the center of mass (COM) for $Fe(CN)_6^{4-}$ ion. The well-defined minimum of PMF was different for these two kinds of electrodes, as shown in Figure 5c (≈ 0.40 nm for LDHs and ≈ 0.65 nm for GRA). Furthermore, the free energy of $Fe(CN)_6^{4-}$ ion near the GRA was around -3.6 kJ mol⁻¹. However, the situation was different for Fe(CN)_6^4-

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Figure 5. MD simulations reveal the advantages of LDH electrode for the sorption of $Fe(CN)_6^{4-}$ ions. a) The snapshot of models for LDH (without showing K⁺, Na⁺, and OH⁻). b) The number density (ρ_n) of nitrogen atoms in $Fe(CN)_6^{4-}$ ions as a function of distance from the electrode (note that planes across centers of surface atoms of LDH and GRA electrodes are located at z = 0 nm). c) Tendency for the sorption of $Fe(CN)_6^{4-}$ ion at electrodes. d) The force on the harmonic spring during steered MD separation of $Fe(CN)_6^{4-}$ ions and electrodes.

ion near the LDHs. A deeper potential well appeared from 0.70 to 3.75 nm (around -5.6 kJ mol^{-1}), suggesting the preferential proximity of Fe(CN)₆^{4–} ions to the LDHs electrode surface. This process for Fe(CN)₆^{4–} ion dissociating from the electrode, was also visible in the force on the harmonic spring during steered MD simulations(Figure 5d).

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To investigate the electrochemical performance and stability of LDH-CF, we used a flow cell for demonstration and assembled it for a charge-discharge test (Figure \$9, Supporting Information). CF and LDH-CF were installed as the positive electrodes in the batteries, respectively. The carbon felt electrode was sandwiched between two graphite plates engraved with the serpentine flow field (Figure 6a). The AZIFB equipped with LDH-CF had outstanding performance based on the excellent ion transport ability of LDH-CF. Figure 6b presents the rate performance of the two batteries assembled with CF and LDH-CF, respectively. The LDH-CF enabled the battery with a higher VE than that of CF at current densities ranging from 80 to 320 mA cm⁻². The difference in performance became more pronounced with an increase in the current density. When the current density reached as high as 320 mA cm⁻², the VE of the AZIFB with LDH-CF demonstrated an improvement exceeding 10%. This indicated that AZ-IFB assembled with LDH-CF had lower voltage and energy losses during the charging and discharging processes, mainly due to the enhanced mass transfer ability of the electrode by LDH-CF, which reduced the concentration polarization of the battery. At high current densities, the concentration polarization of the battery became more significant due to accelerated reaction rates,

making the enhancement effect of LDH-CF more pronounced. Moreover, even at an ultra-high current density of 320 mA cm⁻², AZIFB assembled with LDH-CF could maintain a VE of over 81%, providing an important foundation for increasing the current density of AZIFBs. To further analyze voltage losses in the battery, we measured the polarization losses and peak power densities at different SoCs. Concentration polarization began to dominate in polarization curves as the current density increased. As shown in Figure 6c and Figure S10 (Supporting Information), the AZIFB with LDH-CF had lower voltage losses and higher limiting current density. The high working current density and high working voltage provided AZIFB with a higher peak power density. At 80% SoC, the peak power of the battery could reach 952 mW cm⁻². The cycle performance of the battery was tested at 80 and 240 mA cm⁻², respectively (Figure 6d; Figure S11, Supporting Information), to test the stability of LDH-CF in the battery. The cyclic CE, VE, and EE are shown in Figure 6e,f. The stable voltage curve (Figure 6d) and discharge capacity verified the stability of LDH-CF in the battery. At a current density of 80 mA cm⁻², the battery maintained a VE of 93.2% and an EE of nearly 90% over >200 cycles. Even at a current density of up to 240 mA cm^{-2} , the battery maintained a CE of 98.2%, a VE of 85.9%, and an EE of 84.3% over 375 cycles, which is the highest efficiency reported to date (Figure 6g). The variations in experimental conditions and battery structures are listed in Table S1 (Supporting Information). Although other studies have used different battery setups, this comparison still highlights the excellent performance of this work. A critical factor affecting VE is the membrane type.

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Figure 6. a) Photograph of the serpentine flow field. b) VE of AZIFB with CF or LDH-CF positive electrode under different current densities. c) Polarization and peak power density of AZIFB with LDH-CF positive electrode at different *SoCs*. d) Voltage profiles of AZIFB with LDH-CF positive electrode under 80 mA cm⁻². CE, VE, and EE of AZIFB with LDH-CF positive electrode under e) 80 mA cm⁻² and f) 240 mA cm⁻². g) Plot of VE versus current density in different literatures.

Although the SPEEK membrane used in this study has certain advantages, it still has the highest VE even under the same membrane type. This can be attributed to the enhancement of the ion mass transfer process on the electrode surface. Irrespective of the battery setup, this study demonstrates the highest level of performance. The stability of LDH-CF was determined by examining its morphology of LDH-CF after cycling. The SEM images revealed that the LDHs grew stably on the surface of the carbon fiber and maintained a dense and uniform distribution after long-term cycling (Figure S12, Supporting Information). Benefiting from the mass transfer enhancement, LDH-CF can significantly improve battery performance, reduce voltage and energy losses, and raise the upper limit of the battery operating current density, achieving high EE at ultra-high current densities.

3. Conclusion

In conclusion, this study presented an innovative approach to enhance the mass transfer abilities of flow batteries through the in

situ growth of an array of LDHs nanosheets with abundant mesoporous structures on a carbon felt substrate.

By leveraging the positive charge characteristics of the LDHs main layer and the mesoporous structure of the fiber surface, LDH-CF effectively enhanced ion transfer at the electrode surface. When applied as the positive electrode in an AZIFB, LDH-CF demonstrated exceptional performance across various current densities. At a current density of 80 mA cm⁻², the AZIFB utilizing the LDH-CF material exhibited remarkable performance, maintaining a VE of 93.2% and an EE of over 90%. Even at an ultra-high current density of 320 mA cm⁻², the system achieved an EE of 80%, surpassing the performance reported in previous studies. Moreover, the AZIFB incorporating LDH-CF demonstrated an impressive EE of 84.3% over 375 cycles at a high current density of 240 mA cm⁻².

Specifically, the findings of the present study are expected to provide significant insights into enhancing the working current density of flow batteries, marking an important step toward the widespread application of zinc-based flow batteries

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at a large scale. Given its ability to improve mass transfer and deliver high performance under various operating conditions, the LDHs nanosheet array with mesoporous structures grown on carbon felt is a promising material for future developments in flow battery technology. The affordability, non-toxicity, harmlessness, and longevity of LDHs preparation materials further suggest its potential for sustainable and circular economic applications.

4. Experimental Section

Materials: Sodium ferricyanide and zinc oxide were purchased from Shanghai Macklin Biochemical Technology Co., LTD. Sodium hydroxide, potassium hydroxide, urea, aluminum nitrate hexahydrate, and magnesium nitrate hexahydrate were provided by Sinopharm Chemical Reagent Co., LTD. These reagents were supplied with an analytical grade (AR). The carbon felt was GFA3 (3 mm thickness) from SGL Carbon. The membrane was prepared by the phase inversion method. The poly (ether sulfone) (PES) and minor amount of sulfonated poly (ether ether ketone) (SPEEK) polymers (the total concentration of the polymers was 35 wt.% and the SPEEK content in the polymers was 10 wt.%) were first dissolved in DMAc, then casted the above solution onto a clean glass plate followed by immersing it into the water to form the PES porous substrate.

Preparation of MgAl-LDH Carbon Felt: The MgAl layered double hydroxides were synthesized by the co-precipitation method of urea hydrolysis. In a typical procedure, 10.28 g Mg(NO₃)₂·6H₂O, 7.50 g Al(NO₃)₃·9H₂O, and 33.6 g urea were dissolved in 100 mL deionized water by stirring. A piece of carbon felt (CF, 5 cm × 5 cm × 3 mm) was immersed in the solution for 12 h to saturate the porous carbon felt. The carbon felt and solution were transferred together to a 200 mL Teflon-lined hydrothermal reactor. The reactor was maintained at 130 °C for 10 h to produce LDH-coated carbon felt (LDH-CF). After cooling the reactor, the reacted carbon felt was removed from the reactor and washed in the deionized water. The carbon felt was vacuum-dried at 60 °C for 8 h. Meanwhile, the remaining white hydrotalcite in the reactor was also collected and freeze-dried into powder.

Samples Characterization: Field-emission scanning electron microscopy (SU-8010, X-max80, Japan) and energy-dispersive X-ray spectroscopy were used to detect the morphologies and structures of the prepared electrodes. Transmission electron microscopy (HT7700, Japan) was used to characterize the morphology and crystal structure of the synthesized LDHs. LDH-CF fixed to the glass sheet was also photographed by an atomic force microscope (Bruker Dimension Icon, German), and a 3D phase diagram was generated to show the electrode's surface morphology. X-ray diffractometer (Ultimate IV, RIGAKU, Japan) with a monochromatic Cu K α radiation source at 40 kV and 40 mA and a scan rate of 2 min⁻¹ was used to identify the composition and crystal structure of LDH-CF in the 5°-90° scan angle range. Fourier infrared spectroscopy (Thermo Scientific Nicolet iS20, USA) and X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha, USA) were used to detect the component difference between the LDH-CF and the original carbon felt. The infrared spectrum of the sample was collected under the conditions of a resolution of 4 cm^{-1} , with the scan times being 32 and the test wave number ranging from 400 to 4000 cm⁻¹. The contact angle measuring device (Dataphysics, German) was used to photograph and measure the contact angle of the positive electrolyte on the electrode surface. Nanoparticle size and Zeta potential analyzer (Malvern Zetasizer Nano ZS90, UK) were used to detect the zeta potential value of the sample in an aqueous solution.

In addition, the pore structure of the carbon felt before and after modification was also tested. An automatic surface area analyzer (Micromeritics ASAP 2460, USA) was used to detect micropore and mesoporous distribution of samples as well as specific surface area. The specific surface area of the sample was obtained from the isothermal desorption curve using BET method after the adsorption and desorption of 77 K liquid nitrogen. A high-performance automatic mercury injection instrument (Micromeritics AutoPore V 9620, USA) was used to detect micrometer pores of samples.

Electrochemical Measurement: Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were performed on a VMP-3 electrochemical workstation (Biologic, France). A typical three-electrode cell was used for testing, with the sample clamped between a glassy carbon electrode as the working electrode, a saturated calomel electrode as the reference electrode, and a platinum mesh as the counter electrode. The tests were conducted in 80 mL 0.2 mol L⁻¹ Fe(CN)₆⁴⁻ + 2 mol L⁻¹ OH⁻. To avoid Faradaic currents, the voltage range for the CV test was selected within 0–0.1 V(vs SCE), and the scan rate ranged from 10 to 100 mV s⁻¹. The frequency range for EIS was selected from 200 kHz to 100 MHz.

Battery Test: The synthetic LDH-CF was mounted on the positive side of the flow battery, and the original carbon felt was used as the electrode on the negative side. The area of the carbon felt was 25 cm². Two graphite plates with the serpentine flow field were used as current collectors. The negative and positive electrolytes were 60 mL 0.4 mol L^{-1} $Zn(OH)_4^{2-} + 3.8 \text{ mol } L^{-1} OH^- \text{ and } 60 \text{ mL } 0.8 \text{ mol } L^{-1} Fe(CN)_6^{4-} + 3 \text{ mol}$ L⁻¹ OH⁻, respectively. The charge and discharge tests were performed on the CT-4008Tn tester (Neware, China). The charge and discharge mode was constant current charge and discharge under different current densities (80–320 mA cm⁻²). In order to obtain the rate performance of the battery, three cycles were conducted under each current density. To obtain the cycle performance of the battery, long-term charge-discharge cycles were conducted under current densities of 80 and 240 mA cm⁻², respectively. Charging capacity was controlled by charging time. The discharge process was cut off when the voltage reached 0.1 V. Polarization curve measurements were performed on a VMP-3 electrochemical workstation (Biologic, France) with a 100 A current amplifier. The polarization curves were measured when the state of charge was controlled at 20%, 50%, and 80% respectively

Calculation of Flow Rate: The detailed flow rate calculation procedure was referred to $\text{Ref}.[^{[41}]]$

$$I = nFQC \times \min\{SoC, 1 - SoC\}$$
(1)

$$Q_{ac} = fac \times Q \tag{2}$$

where I, n, F, Q, C, SoC, fac and Q_{ac} are the current, number of transfer electrons, faraday constant, minimum flow rate, concentration of reactive ions, state of charge, flow rate expansion factor, and actual flow rate, respectively. In order to ensure a low concentration polarization loss, a certain magnification fac was applied to the minimum flow rate Q.

Calculation of Mass Transfer Coefficient: The mass transfer coefficient was calculated by limiting current method. When the reactive ions on the electrode surface were exhausted, the overpotential increased sharply, and the current at that time was termed as the limiting current. The mass transfer coefficient of the reactive ions in the diffusion layer can be calculated according to Fick's law. The calculation equation is as follows:

$$I_{\rm lim} = nFak_{\rm m}c_0 \tag{3}$$

where l_{lim} (Am⁻³),n,F(C mol⁻¹),a(m²m⁻³), k_m (ms⁻¹), c_0 (molL⁻¹) are the limiting current per unit volume, number of transfer electrons, faraday constant, specific surface area per unit volume, mass transfer coefficient and concentration of reactive ions, respectively.

Given the difference in the specific surface area of the materials, ak_m rather than k_m was used to represent the actual mass transfer capacity of the surface of the different materials.

Molecular Dynamics and Optimization: All molecular dynamics (MD) simulations were performed by the GROMACS software.^[42] The starting configurations were generated with the PACKMOL software.^[43]

Two kinds of boxes were built: one containing two LDH sheets (xyplane) on each border (z-side) of the box as a model of the working electrodes and another one containing two graphene sheets. Their length in the x-direction and y-direction of the graphene sheets was 6.4 and 3.7 nm, respectively. The total length of the electrolyte was 11.1 nm in the z-direction inside the electrode gap, containing ion pairs number of Na₄Fe(CN)₆ and KOH for 144 and 532, respectively, and 8100 water molecules as solvent. The ions number in the simulation was calculated close to the real solution concentration in experiments. The force field for Fe(CN)₆^{4–} was based on the intramolecular parameters derived from the Universal Force Field (UFF).^[44] The UFF-based force field has been proven to be suitable for metal complexes. The structures of Fe(CN)₆^{4–} were optimized in Gaussian 09 software using TPSSh/def2-TZVP method.^[45] The electrostatic potential involved in the analyses was evaluated by Multiwfn software.^[46] The LDHs mineral was modeled using the CLAYFF force field.^[47]

The NVT ensemble was used with a Nose–Hoover thermostat to maintain the temperature at 298 K.^[48,49] A cutoff distance of 1.2 nm was employed for the van der Waals term via direct summation. The long-range electrostatic interactions were computed via PME method.^[50] An FFT grid spacing of 0.16 nm and cubic interpolation were used to compute the electrostatic interaction in the reciprocal space. A cutoff length of 1.2 nm was adopted in the calculation of electrostatic interactions in real space. The leapfrog integration algorithm was taken to solve the equations of motion with a time step of 2 fs. The system was relaxed in the NVT ensemble for at least 50 ns, and data were collected for 50 ns. The atoms were visualized in figures using the open-source visual MD (VMD).^[51]

PMF represented the variation of free energy and was evaluated by the umbrella sampling method.^[52] A series of initial configurations were generated from the force on the harmonic spring during steered molecular dynamics, and each of them corresponded to a location where the molecule was restrained via a harmonic potential. It could be understood as the molecule being bound by a spring and moving back and forward around a given position, traveling freely along the plane parallel to the electrode surface. Rather than being fixed, the molecule was allowed to rotate, experiencing all possible orientations. With the weighted histogram analysis method,^[52] the PMF was subsequently extracted. To determine the PMF profile for Fe(CN)₆^{4–}, one Fe(CN)₆^{4–} ion was added into the system with LDHs or GRA electrode, since the PMF for one particle was enough to reveal its free energy distribution and the origin of its density distribution.^[39,40] In order to maintain electrical neutrality for the system, sodium ions were proportionally reduced.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

alkaline flow battery, energy storage, ion transport, layered double hydroxides, mesoporous materials

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