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aqueous-batteries- applications-for- pair-dancing- proton-transfer-in- ultrahigh-rate-and

Ultrahigh-rate and ultralong-life aqueous
batteries enabled by special pair-dancing
proton transfer



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Ultrahigh-rate and ultralong-life aqueous batteries
enabled by special pair-dancing proton transfer review

PDF Version of the webpage (first pages)

<https://salgenx.com/aqueous-batteries-applications-for-pair-dancing-proton-transfer-in-ultrahigh-rate-and-ultralong-life-energy-storage.html>

Review of Ultrahigh-rate and ultralong-life aqueous batteries enabled by special pair-dancing proton transfer

Abstract

The design of Faradaic battery electrodes with high rate capability and long cycle life comparable to those of supercapacitors is a grand challenge. Here, we bridge this performance gap by taking advantage of a unique ultrafast proton conduction mechanism in vanadium oxide electrode, developing an aqueous battery with untrahigh rate capability up to 1000 C (400 A g⁻¹) and extremely long life of 0.2 million cycles. The mechanism is elucidated by comprehensive experimental and theoretical results. Instead of slow individual Zn²⁺ transfer or Grotthuss chain transfer of confined H⁺, the ultrafast kinetics and excellent cyclic stability are enabled by rapid 3D proton transfer in vanadium oxide via the special pair dance switching between Eigen and Zundel configurations with little constraint and low energy barriers. This work provides insight into developing high-power and long-life electrochemical energy storage devices with nonmetal ion transfer through special pair dance topochemistry dictated by hydrogen bond.

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Grotthuss proposed a chain mechanism to explain the movement of hydrogen atoms

Over two centuries ago, Grotthuss proposed a chain mechanism to explain the movement of hydrogen atoms (21). As illustrated in Figure 1A, this mechanism was later revisited to describe proton mobility when ions and protons were discovered. In this process, a proton, acting as a bridge between two water molecules, switches between the molecules, displacing one hydrogen atom from its original molecule and triggering a sequence of similar displacements (22, 23).

However, recent theoretical studies (24–27) have challenged the notion that proton transfer follows a simple chain mechanism. As depicted in Figure 1 (B and C), it is now understood as a complex hierarchical process involving multiple steps and time scales. This process includes partner exchange, selection, rattling, and settling into a new Eigen configuration. The activation enthalpy for proton transfer is particularly important during the selection step, which allows the formation of the distorted Zundel intermediate. The special pair dance mechanism introduces randomness in the proton hopping direction, resulting in three-dimensional (3D) diffusive proton transfer behavior. This randomness reduces constraints on proton transfer and lowers the energy barrier.

Consequently, preserving this unique transfer mechanism is essential for maintaining the intrinsic mobility of protons in cathodes and improving the electrochemical kinetics of faradaic battery electrodes.

Batteries equipped with this vanadium oxide cathode exhibit a remarkable combination of high energy density, akin to metal-ion batteries, and high power density and long cycle life, similar to supercapacitors

In numerous inorganic cathode materials, the lattice spacing is too narrow to accommodate an adequate number of water molecules for proton solvation. This limitation significantly hampers the exchange and selection processes of protons with water molecules. Consequently, the unique special pair dance mechanism is ineffective in these electrode materials. Additionally, ultrafast infrared measurements and theoretical studies (28–30) reveal that the dynamics of solvent water molecules are notably slowed down within such confined volumes. Both the insufficient solvation and sluggish dynamics of confined water molecules contribute to sluggish proton transfer kinetics in cathodes where proton (de)insertions are known to play a role (31, 32).

Recognizing the pivotal role of solvation structure and proton dynamics in proton transfer kinetics, we have developed a layered hydrated vanadium oxide cathode material that incorporates an abundance of lattice water. This design allows for a hierarchical and multidirectional concerted cleavage and formation of hydrogen bonds (HB), facilitating the rapid movement of H^+ ions through the special pair dance mechanism. While there are no previous instances of such a unique mechanism occurring in vanadium oxide cathodes, molecular dynamic simulations and nudged elastic band calculations strongly support its existence in our vanadium oxide material. This breakthrough significantly enhances the charge transfer kinetics, subsequently adjusting the ratio of H^+/Zn^{2+} as charge carriers depending on the charge/discharge rate.

As a result, batteries equipped with this vanadium oxide cathode exhibit a remarkable combination of high energy density, akin to metal-ion batteries, and high power density and long cycle life, similar to supercapacitors. These batteries achieve an extraordinary feat, boasting an ultralong cycle life of 0.2 million cycles at 500 C (200 A g^{-1} , 80 mA cm^{-2}) with a power density of 162 kW kg^{-1} at an energy density of 103.6 Wh kg^{-1} (based solely on the mass of the cathode's active material).

Results

As depicted in Figure 1H, the optimal quantity of interlayer water molecules in each unit cell of wet NZVO ($1\text{Na}_2\text{Zn}_{16}\text{V}_{40}\text{O}\cdot 20\text{H}_2\text{O}$) is 20, consisting of 10 free water and 10 ligand water molecules, randomly distributed. Subsequent to this, DFT calculations were employed to identify energetically favorable configurations for assemblies of water molecules confined within the V_2O_5 layers. Upon relaxation, the free water and ligand water collectively form a hydrogen bond (HB) network (Figure 1I). Given the differing crystallographic positions of Na^+ and Zn^{2+} , various models of NZVO with diverse arrangements of Na^+ and Zn^{2+} were considered (see fig. S10). The model with the lowest total energy, depicted in Figure 1H, corresponds to the most stable structure of NZVO. The calculated results reveal a characteristic layered structure within the triclinic system (see table S2).

Within the interlayer of NZVO, the interlayer free water, ligand water (spanning approximately two layers of water), and two layers of terminal oxygen coordinated with V collectively establish a 3D interconnected and dense HB network. This network extends approximately 0.67 nm in height along the c-axis and infinitely within the 2D a-b plane (Figure 1I). The 3D continuous and abundant HB network provides an essential solvation environment for protons. This environment facilitates a hierarchical and multidirectional concerted cleavage and formation of hydrogen bonds, enabling the rapid transport of H^+ ions through the special pair dance mechanism. This mechanism involves switching between Eigen and Zundel configurations with minimal constraints and low energy barriers.

The ligand water, strongly bound to Zn^{2+} or Na^+ , collaborates with these cations to serve as pillars within the host framework. This plays a critical role in stabilizing the HB network, preventing structural stress and failure, and ensuring long-term cycle stability. Conversely, the free water, possessing high mobility, can rapidly adjust its orientation to reconstruct HB network orientations and configurations, facilitating fast proton conduction.

Summary of Process

To summarize, the proton transfer mechanism within NZVO adheres to the Eigen-Zundel-Eigen process, similar to bulk water, facilitated by the special pair dance (as illustrated in Figure 3H and movie S1). The special pair dance effectively introduces rapid randomization of proton hopping directions, transforming the proton transfer within interlayer-confined water into a random walk-diffusive process. This differs significantly from the coherent transfer envisioned by Grotthuss, which involved a chain-like progression of water molecules.

Electrochemical Performance of Zn/NZVO Batteries

Thanks to the ultrafast charge transfer kinetics facilitated by the unique proton special pair dance mechanism, the Zn/NZVO battery demonstrates exceptional rate capability. It delivers impressive capacities of 436, 410, 397, 374, 357, 325, 268, 205, 155, 118, and 92 mA h g⁻¹ at rates ranging from 0.5 C to 1000 C (as shown in Figure 5A). The corresponding charge and discharge profiles at various rates can be seen in Figure S30. Furthermore, even when the rate dramatically drops from 1000 C to 0.5 C, the discharge capacity rebounds to 457 mAh g⁻¹, indicating the robust structural integrity of the NZVO electrode.

At an astonishingly high rate of 1000 C, the Zn/NZVO battery can complete a full charge/discharge cycle in less than 2 seconds. This level of high-rate performance is comparable to that of electrodes in capacitors and outperforms the majority of Faradaic electrodes. The remarkable high-rate performance is also evident in the Ragone plot (Figure 5B). The Zn/NZVO battery attains an energy density of 315.3 Wh kg⁻¹ at a power density of 146.9 W kg⁻¹ and maintains an energy density of 103.6 Wh kg⁻¹ at an extremely high power density of 162 kW kg⁻¹ (based on the mass of NZVO). These achievements surpass the performance of previously reported aqueous proton and Zn-ion cells/capacitors (as detailed in tables S4 and S5) (12, 20, 37, 45–52).

DISCUSSION of Science Article

In summary, we have successfully developed an aqueous battery that exhibits remarkable improvements in rate capability and cycle life compared to previous Faradaic batteries. Our extensive experimental and theoretical findings highlight the significance of a 3D dense hydrogen-bonding network in providing a crucial solvation environment for protons. This environment enables rapid transitions between the Zundel and Eigen configurations and facilitates three-dimensional diffusion with minimal energy barriers and volume changes. The unique special pair dance mechanism bestows protons with significantly faster transfer kinetics when compared to the sluggish kinetics of metal cations like Zn^{2+} . Furthermore, the minimal volume change during proton transfer effectively prevents structural stress and failure resulting from electrochemical cycling. These two factors, in isolation, contribute to the high power density reminiscent of supercapacitors and the impressive long-term cycling stability.

While Zn^{2+} plays a role in charge transport, its contribution becomes negligible at high rates. Another notable feature arising from this unique proton transport mechanism is that the overall battery performance is nearly unaffected by the choice of anion in the electrolyte, a crucial practical advantage. This work provides valuable insights into the development of high-power and long-life electrochemical energy storage devices that rely on non-metal ion transfer through the special pair dance topochemistry governed by hydrogen bonding. The occurrence of this special pair dance topochemistry depends on the presence of a dense and interconnected hydrogen-bonding network. Therefore, future electrode material design should prioritize a large interlayer distance (>1 nm) and a substantial medium presence to enable this special pair dance topochemistry and achieve high power density.

To enhance the practical applicability of Zn/NZVO batteries, increasing energy density is a key consideration. One approach involves introducing electron-withdrawing groups, such as PO_4^{3-} and F^- , into the host structure to elevate the average operating voltage, thereby boosting energy density. Additionally, designing a hierarchical porous structure offers the potential to improve both compaction density and kinetic properties by facilitating rapid ion transport and mitigating diffusion limitations throughout the entire electrode. This avenue warrants further exploration in future research endeavors.

Application to Salgenx Flow Batteries

Instead of Zn/NZVO batteries, we are experimenting with Zn/NZXO batteries. The X denotes a material which is proprietary.

We are considering our standard saltwater flow battery using water and oil electrolyte carriers for the Hydrogen storage while using cathode materials for the NZXO.

A battery of this configuration would not be suitable for desalination, graphene production, or other simultaneous charging functions.
