Enabling safe aqueous lithium ion open batteries by suppressing oxygen reduction reaction

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Due to the non-flammable nature of water-based electrolytes, aqueous lithium-ion batteries are resistant to catching fire. However, they are not immune to the risk of explosion, since the sealing structure adopted by current batteries limits the dissipation of heat and pressure within the cells. Here, we report a safe aqueous lithium-ion battery with an open configuration using water-in-salt electrolytes and aluminum oxide coated anodes. The design can inhibit the self-discharge by substantially suppressing the oxygen reduction reaction on lithiated anodes and enable good cycle performance over 1000 times. Our study may open a pathway towards safer lithium-ion battery designs.
The safety of lithium-ion batteries (LIBs) has raised significant concerns in recent years due to several fire-related incidents. The fully charged LIB consists of a highly energetic transition metal oxide cathode and a lithiated graphite anode in intimate contact with a flammable organic electrolyte. Any abuse by overcharging, external short-circuiting, or crushing can trigger spontaneous heat-generation. This exothermic event can result in thermal runaway, or even explosion due to high internal cell pressure producing fire and toxic gases. The thermal stability of batteries depends on the electrolyte’s flammability and its ability to dissipate the heat and pressure. Currently, all commercial LIBs are in sealed configurations to protect the highly reactive electrodes and liquid electrolytes from reacting with the moisture and the reactive gases in the air, inherently limiting the dissipation of heat and pressure (Fig. 1a). Although many safety devices, such as safety vents, thermal fuses, circuit breakers, positive temperature coefficient elements, and shutdown separators, have been applied to LIBs and battery packs, the fire and explosion risks of LIBs are still present. To make LIBs intrinsically safe, the LIB’s chemistry and configuration have to be changed.

At the chemistry level, the volatile, flammable, and toxic organic electrolytes in commercial LIBs should be replaced by non-flammable aqueous electrolytes. However, the traditional non-flammable aqueous LIBs suffer from a low energy density due to the narrow electrochemical stability window of aqueous electrolytes. The performance of aqueous LIBs is significantly impacted by the dissolved O$_2$ in electrolytes from the air through the oxygen reduction reaction (ORR). Xia and coworkers have demonstrated that any discharged negative electrode in an aqueous LIB would react with O$_2$, resulting in the marked capacity fading. Sealing cell can help to eliminate the O$_2$ and can significantly improve the battery performance. But sealed aqueous LIBs still have the risk of thermal runaway and explosion when the internal cell pressure quickly rises, either by electrochemical water decomposition or uncontrolled high-temperature thermovaporization, as observed in sealed aqueous Ni-MH and VRLA (valve regulated lead acid) batteries. The battery’s vents are not always able to prevent cell explosions because the pressure builds up from accelerated side reactions producing gas at a rate too fast for the safe operation of the safety valves, leading to the dangerous cell explosions. The sealed aqueous LIBs have to be replaced by an open configuration design due to their superior ability to dissipate heat and pressure. To our best knowledge, such open configuration aqueous LIBs have not been demonstrated yet. Recently, we developed a “water-in-salt electrolyte” (WiSE) that significantly reduced the O$_2$ solubility in the electrolyte and expanded the electrochemical stability window of aqueous electrolytes from 1.5 to >3.0 V. The WiSE enabled the energy density of aqueous LIBs to be significantly enhanced from 75 Wh kg$^{-1}$ to over 300 Wh kg$^{-1}$ (on the material level). The uniqueness of WiSE has been extensively reviewed by Eftekhar.

Here in this study, we report intrinsically safe LIBs with an open configuration. It is found that the O$_2$ solubility markedly decreases in the electrolytes from 1.97 mg L$^{-1}$ in 1 m “salt-in-water electrolytes” (SiWE) (1 m Li$_2$SO$_4$) to 0.95 mg L$^{-1}$ in 28 m WiSE (21 m LiTFSI + 8 m LiOTf, mol per kilogram), and further reduces to 0.19 mg L$^{-1}$ in 63 m WiSE, significantly suppressing the ORR on lithiated anodes. The ORR on lithiated anodes can be further inhibited by coating 2.0-mm-thick aluminum oxide (Al$_2$O$_3$) layer on anodes. Furthermore, the 28 m WiSE can prevent water evaporation even at a high temperature of ~100 °C due to the strong hydrophilic property of the LiTFSI salt. The LiMn$_2$O$_4$/Al$_2$O$_3$/LiTi$_2$(PO$_4$)$_3$ open power cell with 28 m WiSE demonstrates an energy density of 62.4 Wh kg$^{-1}$ and a stable cycle life of >1000 cycles. The 0.1 Ah LiVPO$_4$F//Al$_2$O$_3$/Li$_4$Ti$_5$O$_12$ open pouch cell with 63 m WiSE (42 m LiTFSI + 21 m Pyr$_1$(TFSI) yield an energy density of 170 Wh kg$^{-1}$ and a high energy efficiency of 92.8% for over 50 cycles.

**Fig. 1** The safety of commercial LIB and the oxygen reduction reaction (ORR) in the “water-in-salt electrolytes” (WiSE) and the “salt-in-water electrolytes” (SiWE). a Typical thermal runaway in a Li-ion cell with sealed-configuration. b Solubility of O$_2$ in aqueous electrolytes. c Linear sweep voltammetry (LSV) of carbon black in the O$_2$-saturated 1 m SiWE at a scan rate of 10 mV s$^{-1}$ with different rotating disk electrode (RDE) rotation rates. d LSV of carbon black in the O$_2$-saturated 1 m SiWE and the corresponding ring current for the oxidation of hydrogen peroxide at a scan rate of 10 mV s$^{-1}$ with a disc surface area of 0.2475 cm$^2$, a rotating ring disk electrode (RRDE) collection efficiency of 0.37, and an electrode rotation rate of 1600 rpm. e LSV of carbon black in the O$_2$-saturated 28 m WiSE at a scan rate of 10 mV s$^{-1}$ with different RDE rotation rates. f LSV of carbon black in the O$_2$-saturated 28 m WiSE and the corresponding ring current for the oxidation of peroxide at a scan rate of 10 mV s$^{-1}$ with a disc surface area of 0.2475 cm$^2$, an RRDE collection efficiency of 0.37, and an electrode rotation rate of 1600 rpm. g The mass retention of the 28 m WiSE in the air at room temperature with a relative humidity of ~68%. h The mass retention of the 28 m WiSE at different temperatures for 30 min.
Results

WISE enabled open configuration. The low O₂ content in the 28 m WiSE reduces the ORR kinetics at the electrodes. In order to build an open aqueous battery, the ORR kinetics at the electrodes must be reduced. The gas solubility in a solvent can be largely reduced by increasing the salt concentration in the solvent. Figure 1b shows that the solubility of O₂ in the water markedly decreases from 1.97 mg L⁻¹ in the 1 m SiWE to 0.95 mg L⁻¹ in the 28 m WiSE, further down to 0.21 mg L⁻¹ in the 35 m WiSE (35 m NaFSI in H₂O), and even further to 0.19 mg L⁻¹ in the 63 m WiSE. When an ionic salt is added to water, the dissolved ions will attract the water molecules due to ion solvation. The solvation of ions by water will reduce the affinity of dissolved non-polar O₂ to water, thus reducing the solubility of O₂ in water. The low O₂ content in electrolytes reduces the ORR kinetics at the electrodes. Using carbon black as a model electrode (the most reactive component in conventional anodes), the ORR performance of carbon black in the O₂-saturated 28 m WiSE and in the O₂-saturated 1 m SiWE were investigated using the RDE technique. The ORR kinetics on carbon black were significantly reduced with the increase of salt concentration in O₂-saturated aqueous electrolytes, as demonstrated by three pieces of evidence in RDE measurements at 1600 rpm (Fig. 1c, e): (1) The onset of the ORR potential at carbon black electrodes, where the reduction current increases sharply, (−0.3 V vs. Ag/AgCl) in the 28 m WiSE (Fig. 1e) is more negative than the onset ORR potential (−0.2 V vs. Ag/AgCl) in the 1 m SiWE (Fig. 1c); (2) The limiting current of carbon black electrodes in the 28 m WiSE (0.045 mA cm⁻²) is only 4.5% of the limiting current (1.0 mA cm⁻²) in the 1 m SiWE; and (3) The half-wave potential (−0.45 V vs. Ag/AgCl) of the ORR in the 28 m WiSE is much more negative than that (−0.28 V vs. Ag/AgCl) in the 1 m SiWE. The much lower reduction current of the carbon black electrodes in the N₂ saturated 28 m WiSE and 1 m SiWE (Supplementary Fig. 1) than those in the O₂ saturated electrolytes at the same conditions (Fig. 1c, e) confirmed that the currents in Fig. 1c, e are attributed to the ORR.

The low diffusion coefficient in the 28 m WiSE further reduces the ORR kinetics on the electrodes. In addition to decreasing the O₂ solubility, the high salt concentration also reduces the diffusion coefficients of O₂ in the electrolytes. The diffusion coefficients for O₂ in the 28 m WiSE and the 1 m SiWE were calculated using the Koutecky–Levich (K–L) equation (Eq. 1).

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{\nu D_{O_2}^{2/3} C_{O_2}^{2/3}} + \frac{0.62 nF D_{O_2}^{2/3} C_{O_2}^{2/3} \nu^{-1/6} \omega^{1/2}}{j_i}
\]

Where \( j \) is the measured current density; \( j_k \) is the kinetic current density; \( F \) is the Faraday constant (96485 C mol⁻¹); \( D_{O_2} \) is the O₂ diffusion coefficient in the electrolyte; \( C_{O_2} \) is the O₂ saturation concentration in the electrolytes (6.156 × 10⁻⁵ mol L⁻¹ for the 1 m SiWE and 2.968 × 10⁻⁵ mol L⁻¹ for the 28 m WiSE) (Fig. 1b); \( \nu \) is the kinematic viscosity of the electrolyte that is obtained using the viscometer (1.396 mPa s⁻¹ for the 1 m SiWE and 202.44 mPa s⁻¹ for the 28 m WiSE); \( \omega \) is the electrode rotation rate; and \( n \) is the electron transfer number (for the 1 m SiWE, \( n \) can be obtained via the RRDE test using Eq. 2).

\[
n = 4 - \frac{4j_i}{Nj_k} + j_d
\]

Where \( j_d \) and \( j_i \) are the ring and the disk current, respectively, and \( N \) is the collection efficiency (0.37). From the disk currents of the RRDE in Fig. 1d, the electron transfer number (\( n \)) in the ORR in the O₂-saturated 1 m SiWE was determined to be 2.4–2.6 (Supplementary Fig. 2a) using Eq. 2. This value corresponds to 71–80% H₂O₂ (Supplementary Fig. 2b, calculated using Supplementary Eq. 1 in Supplementary Note 1) and 29–20% OH⁻ as the ORR products. Hence, the diffusion coefficient of O₂ (\( D_{O_2} \)) in the O₂-saturated 1 m SiWE was determined to be 5.45 × 10⁻⁵ cm² s⁻¹. In addition, the ORR products (both H₂O₂ and OH⁻) produced at carbon electrode surface quickly diffuse into the 1 m SiWE and diffuse away from the electrode due to their high solubility and diffusivity, further accelerating the ORR kinetics.

In contrast, the main ORR product on the carbon electrode in the O₂-saturated 28 m WiSE is Li₂O₂, which has been confirmed by the two clear Li₂O₂ peaks in the Raman spectrum of the discharged carbon electrode (Supplementary Fig. 3, Supplementary Note 2). It is consistent with previous reports in other WISE. However, limited H₂O₂ can still be monitored in the O₂-saturated 28 m WiSE (Fig. 1f), suggesting that the H₂O₂ is possibly an intermediate in the ORR. The possible ORR pathway at the carbon electrode in the 28 m WiSE can be best expressed as follows:

\[
\begin{align*}
O_2 + H_2O & \rightarrow HO_2^- + OH^- \\
HO_2^- + H_2O & \rightarrow H_2O_2 + OH^- \\
H_2O_2 + 2OH^- & \rightarrow Li_2O_2 + 2H_2O
\end{align*}
\]
the anode surface, thus reducing the cell self-discharge rate and extending the cell cycle life. However, the formation of this passivation layer on the anode consumes the salts and the Li-ions from the lithiated cathode. To suppress the ORR during the initial passivation layer formation process, an Al2O3 nano-layer was coated on the electrode using ALD to generate an artificial SEI layer prior to cell construction.

The O2 adsorption and the subsequent ORR on the Al2O3 surface were investigated. Figure 3a, b delivers the different charge densities of the O2 adsorbed on the Al2O3 slab. The corresponding adsorption energies (Ead) were calculated using Eq. 6:

\[ E_{ad} = E_{(Al_{2}O_{3}+O_{2})} - E_{(Al_{2}O_{3})} - E_{(O_{2})} \]  

Where the \( E_{(Al_{2}O_{3}+O_{2})} \) is the energy of O2 adsorbed by the Al2O3 slab; \( E_{(Al_{2}O_{3})} \) and \( E_{(O_{2})} \) are the energy of the Al2O3 slab and the O2, respectively. The more negative adsorption energy indicates the stronger O2 adsorption. The typical adsorption energies of the O2 intermediates on Pt, Ni, Pd, Cu, and Ir(111) metals surface are \( -0.72, -1.67, -1.01, -0.56, \) and \( -1.27 \) eV, respectively.25,26 The binding energy of O2 on the O-2 and the Al-surface of Al2O3 are around 0.05 and \(-0.18\) eV, demonstrating the weak interaction between the O2 and the Al2O3 surface and the difficulty in the dissociation of the O2 on the Al2O3 surface.

The RDE curves in Fig. 3c, d confirm that the ORR kinetics at the Al2O3 surface are much slower than the ORR kinetics at the carbon back electrode. Figure 3c shows the LSV of the carbon black and the Al2O3 in the O2-saturated 1 m SiWE, the ORR onset potential of the ORR at the Al2O3 surface is 0.1 V lower than at the carbon black surface. The limiting current density at 1600 rpm at the Al2O3 surface (0.107 mA cm\(^{-2}\)) is only 1/8 of that (0.85 mA cm\(^{-2}\)) at the carbon black surface. Similarly, the Al2O3 also reduces the ORR current in the 28 m WiSE (Fig. 3d). The onset potential of the ORR at the Al2O3 surface is also 0.2 V lower than at the carbon black surface in the 28 m WiSE (Fig. 3d). In addition, the Al2O3 has a fast Li-ion diffusivity27 and the ALD-Al2O3 coating technology has been widely used in industry.

**WISE and Al2O3 enabling low self-discharge anodes.** After assessing the ORR kinetics in the presence of WiSE and Al2O3 coating, further measurements with a model anode are needed to confirm the above results. As the lithiation/delithiation potential of LiTi2(PO4)\(_3\) anode is within the electrochemical stability windows of both the 1 m SiWE and the 28 m WiSE, the LiTi2(PO4)\(_3\) anode was used as a model anode to compare the self-discharge behaviors in the 1 m SiWE and the 28 m WiSE. The Coulombic efficiency of the LiTi2(PO4)\(_3\) in the 1 m SiWE at the current density of 0.5 A g\(^{-1}\) is only 89% (Fig. 4a) and no delithiation capacity is available for the fully lithiated LiTi2(PO4)\(_3\) after 10 h of relaxation at open-circuit in an open-cell (Fig. 4b). The open-circuit potential changed from the fully lithiated potential of \(-0.7\) V to the fully delithiated potential of \(+0.2\) V during 10 h (Fig. 4c). Therefore, the fully lithiated LiTi2(PO4)\(_3\) in the 1 m SiWE has completely self-discharged to LiTif(PO4)\(_3\) after 10 h rest in an open-cell configuration. Supplementary Fig. 4 and Supplementary Note 3 confirm the ORR at the LiTi2(PO4)\(_3\) electrode. Supplementary Fig. 5 and Supplementary Note 4 further confirm the effects of the dissolved O2 in the electrolytes on the self-discharge performance of the lithiuated LiTi2(PO4)\(_3\), the open-circuit potential changed to \(+0.2\) V after only a half hour in a pure O2 atmosphere, while its lithiated potential can be maintained for 50 h without potential increase when the cell was in the absence of O2 (in a N2 atmosphere). Therefore, it can be concluded that the self-discharge of the fully lithiated LiTi2(PO4)\(_3\) in the 1 m SiWE open-cell is proceeds through the following ORR pathway:

\[
O_2 + 4e^- + 2H_2O \rightleftharpoons 4OH^- \tag{7}
\]

\[
O_2 + 2e^- + 2H_2O \rightleftharpoons H_2O_2 + 2OH^- \tag{8}
\]

\[
\text{Li}_{3}\text{Ti}_2(\text{PO}_4)_3 \rightleftharpoons \text{LiTif}(\text{PO}_4)_3 + 2\text{Li}^+ + 2e^- \tag{9}
\]

In an open-cell configuration, the dissolved O2 in the electrolyte receives electrons from the LiTif(PO4)\(_3\) and is reduced into OH\(^-\) or H\(_2\)O\(_2\). As expected, when the Al2O3 nano-layer coated LiTif(PO4)\(_3\) electrode (Supplementary Figs. 6 and 7) is charged/discharged in the 28 m WiSE, the Coulombic efficiency markedly increases to 99.9% (Fig. 4d). The capacity retention of the fully lithiated LiTi2(PO4)\(_3\) after 10 h rest in an open-cell configuration still reaches a high value of >97% (Fig. 4e). Also, the open-circuit potential is maintained at \(-0.5\) V (Fig. 4f) due to the ORR on the lithiated Al2O3@LiTi2(PO4)\(_3\) being significantly inhibited. To further confirm the high ORR suppression capability of the WiSE, a moderate salinity concentration electrolyte of 10 m LiTFSI was also selected to evaluate the self-discharge of the lithiated Al2O3@LiTi2(PO4)\(_3\) anodes. As shown in Supplementary Fig. 8 and Supplementary Note 5, only 52% of the discharge capacity...
remains after 10 h in the 10 m LiTFSI electrolyte, whereas in the 30 m WiSE, the discharged electrode retains over 98% of the initial capacity after a 10 h rest and it maintains over 96% of the initial capacity after 24 h in an open-cell configuration (Supplementary Figs. 9 and 10).

Electrochemical performance of safe WiSE full open cells.
Based on the successfully inhibition of the ORR at the lithiated anode, a full open-cell was designed and fabricated. As the charge/discharge potentials of the LiMn$_2$O$_4$ cathode and the LiTi$_2$(PO$_4$)$_3$ anode are within the electrochemical stability window of both the 28 m WiSE and the 1 m SiWE, the electrochemical performances of the LiMn$_2$O$_4$//Al$_2$O$_3$@LiTi$_2$(PO$_4$)$_3$ open-cell in the 28 m WiSE and the LiMn$_2$O$_4$//LiTi$_2$(PO$_4$)$_3$ open-cell in the 1 m SiWE were compared. The LiMn$_2$O$_4$//Al$_2$O$_3$@LiTi$_2$(PO$_4$)$_3$ open-cell in the 28 m WiSE delivered a capacity of 62.4 Wh kg$^{-1}$ (of total mass of the anode and the cathode) at a rate of 5 C (Fig. 5a) and displayed a high Coulombic efficiency of over 99.9% with a stable cycle life of >1000 cycles (Fig. 5b, c). In sharp contrast, the capacity of the LiMn$_2$O$_4$//LiTi$_2$(PO$_4$)$_3$ open-cell in the 1 m SiWE decreased markedly due to the poor Coulombic efficiency (Supplementary Fig. 11, Fig. 5b, c). Self-discharge is a key issue for all batteries, Supplementary Fig. 12 and Supplementary Note 6 demonstrate that the fully charged LiMn$_2$O$_4$//LiTi$_2$(PO$_4$)$_3$ open-cell with the 1 m SiWE was fully self-discharged by the O$_2$ in the air after 10 h of rest under ambient conditions. The self-discharge performance of the LiMn$_2$O$_4$//Al$_2$O$_3$@LiTi$_2$(PO$_4$)$_3$ open-cell in the 28 m WiSE was measured after resting for 10 h and the fully charged open-cell maintained 96.8% of the initial charged capacity (Supplementary Fig. 13). The capacity retention is still larger than 90% after 15 days of rest (Supplementary Fig. 14). Furthermore, the charging of the LiMn$_2$O$_4$//Al$_2$O$_3$@LiTi$_2$(PO$_4$)$_3$ open cell with a constant capacity can minimize the effect of self-discharge on cycling stability. The constant capacity charge protocol enables the LiMn$_2$O$_4$//Al$_2$O$_3$@LiTi$_2$(PO$_4$)$_3$ open cell in the 28 m WiSE to maintain the same discharge capacity for 100 cycles at a low rate of 1 C, which results in the Coulombic efficiency of the LiMn$_2$O$_4$//Al$_2$O$_3$@LiTi$_2$(PO$_4$)$_3$ open power cell at 1 C reaching >99.7% (Supplementary Fig. 13b). Even at a low rate of 0.2 C, the LiMn$_2$O$_4$//Al$_2$O$_3$@LiTi$_2$(PO$_4$)$_3$ open cell shows a stable discharge capacity for 35 cycles under the constant charge capacity protocol (Supplementary Fig. 15).

To further enhance the cell energy density, a 2.7 V, 0.1 Ah LiVPO$_4$F//Al$_2$O$_3$@Li$_4$Ti$_5$O$_12$ open pouch demo cell was fabricated (Supplementary Fig. 16) using a high voltage LiVPO$_4$F cathode and evaluated in the 63 m WiSE. The 63 m WiSE has a low O$_2$ concentration (0.19 mg L$^{-1}$) and wide electrochemical potential window of >3.15 V (1.76 V – 4.91 V vs. Li$^+$/Li) (Supplementary Fig. 17, Supplementary Note 7). The LiVPO$_4$F//Al$_2$O$_3$@Li$_4$Ti$_5$O$_12$ open pouch cell in the 63 m WiSE was cycled at a rate of 0.2 C and provided 170 Wh kg$^{-1}$ (based on of the total mass of the anode and the cathode) at a rate of 0.2 C. The LiVPO$_4$F//Al$_2$O$_3$@Li$_4$Ti$_5$O$_12$ open pouch cell shows a stable discharge capacity for 35 cycles under the constant charge capacity protocol (Supplementary Fig. 15).
anode and the cathode) (Supplementary Note 8 and Fig. 5d). The cell achieved over 50 cycles with a Coulombic efficiency of 96.8% (Fig. 5e).

Energy efficiency is another critical factor for new battery systems.38,39 We have calculated the energy efficiency of the LiMn2O4/Al2O3@LiTi2(PO4)3 open-cell at the rate of 1 C and found it to be 90% (Supplementary Fig. 13C). The energy efficiency of the LiVPO4F/Al2O3@Li3Ti2(PO4)3 open pouch cell, cycled at 0.2 C, (Fig. 5e) is as high as 92.8%, which is comparable with the value (in the range of 86–98%) of commercial LIBs.29,30 Therefore, the open-cell configuration developed here can satisfy the demand of the market.

To address the potential electrolyte leakage issue in the open-cell design, we added PVA (Poly(vinyl alcohol)) into the 28 m WiSE to form a gel electrolyte. The gel electrolyte can flow when the temperature is increased to 95 °C in order to facilitate battery assembly. When the electrolyte is cooled back to room temperature it forms a solid phase that can eliminate any electrolyte leakage. Supplementary Fig. 18 and Supplementary Note 9 show that the 28 m gel WiSE do not flow at room temperature. As shown in Supplementary Fig. 19b, c, the LiMn2O4/Al2O3@LiTi2(PO4)3 open pouch cell with the 28 m gel WiSE achieved similar electrochemical performance as the cell with the liquid 28 m WiSE. Supplementary Fig. 20, Supplementary Note 10 and Supplementary Movie 1 show that the LiMn2O4/Al2O3@LiTi2(PO4)3 open pouch cell with the 28 m gel WiSE was able to stably power a fan without any electrolyte leakage, even after the pouch cell was cut with scissors.

This aqueous open-cell configuration is a universal design that can also be used in other aqueous batteries. For example, the 35 m WiSE also effectively suppressed the ORR at the discharged electrode, which enabled the intercalated Na3Ti2(PO4)3 electrode in an open-cell configuration to maintain over 98.5% of the initial capacity after resting at open-circuit for 10 h (Supplementary Fig. 21). In addition, the 30 m WiSE also effectively suppressed the ORR at the Zn anode, as demonstrated by the much higher Coulombic efficiency (87.5%) for the Zn plating and stripping in the 30 m WiSE than in the 5 m ZnCl2 SiWE (53%) (Supplementary Fig. 22). The open-cell configuration has several other advantages: (1) some safety devices are not necessary within the cell such as an additional ventilation system; (2) they can be charged at a high voltage setting and high rate; and (3) they have a much lower up-front cost by removing the safety devices and sealing process.

Discussion

The non-flammable aqueous batteries still carry the risk of explosion due to rapidly increasing internal pressure caused by side reaction gaseous products and thermal runaway. The WiSE can effectively suppress the electrolyte evaporation and the ORR reaction at the discharged anode. The ORR at the anode can be further suppressed by coating an Al2O3 nano-layer, which enables the batteries to operate in an open configuration. The LiMn2O4//Al2O3@LiTi2(PO4)3 open power cell achieves a stable cycle life of over 1000 cycles with a low self-discharge rate (90% capacity retention after 15 days). The 2.7 V LiVPO4F//Al2O3@Li3Ti2(PO4)3 open pouch cell achieves a high energy density of 170 Wh kg−1.

The open configuration design provides enhanced resistance to thermal runaway and high-pressure explosion that can markedly improves the safety of LIBs.

Methods

Materials synthesis. LiMn2O4 and Li4Ti5O12 were purchased from MTI. LiVPO4F was supplied by ALees. To synthesize the carbon-coated LiTi2(PO4)3, at first, 100 mL 2 wt% poly-vinyl-alcohol (PVA) aqueous solution was prepared, then Li2CO3, NH4H2PO4, and TiO2 were blended with it. A white solid product was
formed when the water was evaporated after heating at 80 °C with continuous stirring. The product was heated at 900 °C for 10 h at a temperature increasing rate of 5 °C min⁻¹ under the protection of N₂ flow. During the heat-treatment process, it was in a porcelain boat, and the tube furnace was applied. Thermal decomposition vapor-deposition technology was applied to coat carbon on the surface of LiTi₂(PO₄)₂. The as-prepared LiTi₂(PO₄)₂ was placed in a tube furnace and further heated at 780 °C for 2 h, during which, the toluene vapor was carried by N₂ through the tube. The flow rate of N₂ is 1 L min⁻¹. After that, the product was further heated at 900 °C for 2 h under the protection of N₂ without toluene.

**Atomic layer deposition.** The electrodes were coated with Al₂O₃ nano-layer using the atomic layer deposition (ALD) equipment (Beneq TFS 500). The carrier gas was high-purity N₂ with a temperature of 150 °C. 20 precursor pulse cycles of ALD-Al₂O₃ were applied to form 2 nm-thickness layer on the surface of electrodes. During each cycle, alternating trimethylaluminum (4 s, Al precursor) and H₂O (4 s, oxygen precursor) flows were separated by flows of N₂ (4 s for the carrier gas, 10 s for the cleaning gas).

**Electrode preparation and electrochemical measurements.** The working electrodes were prepared by mixing active materials (LiMn₂O₄, LiTi₂(PO₄)₂, LiVPO₄F, or Li₄Ti₅O₁₂), conductive materials (carbon black, CB), and binder PTFE (polytetrafluoroethylene) in a weight ratio of 90:5:5 of active materials/CB/PTFE, then dispersed in a mixture of isopropanol (2.5 mL) and Nafion solution (20 μL); (2) treat the mixture with ultra-sonication for 30 min. After that, the ink (10 μL) was deposited on a glassy carbon disk electrode (RDE or RRDE) and evaporated the solvent in air at room temperature. The electrochemical measurements were performed in a three-electrodes cell at ambient temperature. The RDE or RRDE was used as the working electrode, a platinum electrode as the counter electrode, and Ag/AgCl as the reference electrode. The data was recorded using a Gamry interface 1900.

**Materials characterization.** Raman measurements were carried out by a Horiba Jobin Yvon Labram Aramis using a 532 nm diode-pumped solid-state laser, attenuated to give ~900 μW power at the sample surface. Scanning electron microscopy (SEM) measurements were carried out by Hitachi SU-70 analytical SEM (Japan). Viscosity measurements were carried out using a CANNON-FENSKE viscometer. The surface chemistry of the electrodes after ALD coating was examined by XPS with a Kratos Axis 165 spectrometer. XPS data was collected using a monochromated Al Ka X-ray source (1486.7 eV). The working pressure of the chamber was lower than 6.6 × 10⁻¹⁰ Pa. All reported binding energy values were calibrated to the C 1s peak at 284.8 eV.

**Computational details.** All density functional theory (DFT) calculations were performed using a Vienna Ab Initio Simulation Package (VASP) with projector augmented wave (PAW) method. The exchange–correlation energy is described by the functional Perderw, Burke, and Ernzerhof (PBE) version of the generalized gradient approximation (GGA). The energy cut-off for the plane wave basis is 520 eV. A vacuum layer of 12 Å was used for all calculated models. The energy of O₂ is obtained from the Materials Project. Visualization of the structures are made using VESTA.

**Data availability** The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.
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