Introducing nanomaterials to enhance the performance of lithium batteries

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Abstract. Since human society entered the electrical era, electricity has become an indispensable part in people’s lives, and the battery as the carrier of electricity, whether in the car, or people’s daily lives have a vital role. Since the birth of the first lithium battery, lithium batteries have experienced decades of development, such as the birth of lithium-ion batteries, lithium metal batteries and other types of lithium batteries. However, due to the characteristics of lithium batteries, they still face problems such as low energy density, lithium dendrite growth, reduced Coulomb cycle efficiency, and reversible decrease in capacity. These problems seriously affect the stability and safety of lithium batteries. Therefore, the research has focused on nanotechnology, which brings a good solution to these problems due to the properties of nanoparticles on the microscopic scale. This research summarises the application of nanotechnology in the development of lithium batteries by data analysis, and outlines the current mainstream research directions in several aspects for different types of batteries.

Keywords: lithium batteries; nanomaterials; application.

1. Introduction

The human demand for energy is increasing, where the current widespread use of fossil energy is a non-renewable energy source and their total amount is constantly decreasing, so human society must develop new energy sources in order to develop. In the context of green, energy-saving, emission reduction society, vehicle electrification is revolutionizing the automotive industry. The global electric vehicle (EV) sales exceeded 14 million in 2023, with China accounting for more than 8 million [1]. Although the global EV penetration rate was only 15.8% in 2023, it is expected to grow to about 20% in 2024 [2]. From this point of view, EV has a good prospect, but at the present stage, battery, as an important component in EV, is directly related to the range, service life and safety level of EV. The current low energy density lithium batteries can no longer meet people’s needs, so it urgently needs to develop a new type of high-capacity, high-stability and high-safety lithium batteries to meet the large number of people’s needs.

In recent years, most commercial applications of lithium-ion batteries generally choose graphite as the anode material, resulting in an excellent electrical performance. With the increasingly high requirements for battery energy density, graphite-based battery has been unable to meet the needs of the people [3], and it is to limit the application of graphite electrodes. Therefore, people put their attention on finding anode materials with high energy density. The emergence of crystalline silicon seems to solve people’s problems, because of its ten times the graphite lithium storage capacity, abundant reserves, easy preparation, the occurrence of lithium alloying low potential and other advantages, so that it has become a potential electrode material [4]. However, silicon also has a number of well-known defects, such as the conductivity of intrinsic silicon is not high enough [5], and silicon undergoes a huge volume change, which can cause the large size of silicon broken into small particles, thus affecting the capacity of the battery [6].

For negative electrodes made with lithium metal, each gram of electrodes can carry 3,860 mAh of electrical energy in theory [7]. However, lithium metal anode in the battery is still facing a fatal problem, such as the growth of lithium dendrites. The growth of lithium dendrites will cause irreversible deposition of lithium, a large number of consumed lithium metal, so that the efficiency of the Coulomb cycle is reduced. Lithium dendrites will grow and even puncture the cathode and anode diaphragm, resulting in an internal short-circuit to cause a great danger.

For the much-anticipated Li-S batteries, it shows a high theoretical energy density, which is 7–8 times higher than that of current lithium-ion batteries [8], In addition, sulfur shows some advantages, such as low price, wide distribution and environmental protection, so Li-S batteries have great prospects for development [9]. When lithium in the organic electrolyte undergoes a reduction reaction, it interacts with sulphur to generate polysulphides with high solubility, and the migration of these products leads to the occurrence of the shuttle effect, and the sulphur as the electrode material is even more lost through the above reaction, which increases the loss of the electrode material [10]. The volume expansion during charging and discharging have become important factors limiting the commercial development of lithium-sulfur batteries. The application of nanotechnology provides a good help to the current challenges faced. The application of nanotechnology is committed to solving the following problems, including volume change, SEI membrane, electron/ion transport and atomic/molecular motion. To this end, this research will discuss the application performance of nanotechnology in different types of lithium batteries.

2. Nanomaterials-based lithium-ion batteries

2.1. Nanoporous silicon

The use of crystalline silicon in lithium-ion batteries has significantly increased its lithium storage capacity, and silicon-based electrodes are favoured by virtue of their low lithium alloying/dealloying potentials, long discharge plateaus and abundance. However, silicon shows some limiting problems, where the intrinsic electrical conductivity of silicon is very low and it has a high expansion rate. This can lead to crushing of the electrode structure and considerable capacity degradation, and much research has been carried out at this stage to accommodate this severe volume expansion. There are composites of silicon, in which the carbon-coated silicon-based composites show better performance, carbon and silicon electrodes complement each other, effectively enhancing the conductivity of the material has mitigated the volume expansion during the cycling process [11].

With micron-sized polysilicon particles reactants, a nanoporous structure is chemically etched on the large original silicon particles, and subsequently these nanoporous structures are then reacted with PPAN to prepare a composite electrode. This special nanostructure well mitigates the electrode destruction caused by volume change and does not aggregate due to the presence of voids between different particles, while the presence of PPAN acts as a carbon conductor [11].

When the size of silicon is 100 nm and 1 μm, it has a better electrical performance. Due to the high electrochemical activity of the nanoscale silicon particles caused by the particle agglomeration led to the poor performance of the battery cycle. For 5.5 and 13 μm silicon particles, when the number of cycles reaches 40 times and 10 times, its electrical properties are greatly affected due to the volume expansion of silicon. In the 40th and 10th cycles, the silicon particles undergo expansion and crushing due to the change in their volume, and the larger the size, the earlier their crushing time, leading to a more serious decrease in the Coulomb efficiency. With the continuation of the cycle, the crushed silicon particles present a smaller size, showing a volume effect at smaller sizes, and therefore an increase in the coulombic efficiency, as shown in Fig. 1. As for the silicon particles with a size of 1 μm, despite having better properties such as coulombic cycling, it suffers from a significant volume effect compared to the nano-sized cell, and therefore the performance of this silicon electrode still needs to be improved. In order to improve the defects of the single nanostructure, a nanoporous skeleton was introduced on the micron-sized silicon particles by a metal-assisted chemical etching process.

This technique solves the problem of the agglomeration effect of the nanoparticles by buffering the volume change of the Si particles. Due to the presence of its porous structure, it does not allow for the occurrence of agglomerations unlike that of the simple nanoparticles.

The treated silicon electrodes have the most excellent performance, with CE of 56% and 99% at the 1st and 5th cycles, respectively. Even at 220 cycles, the cell exhibits excellent electrochemical performance. For the first ten cycles, the resistance decreases as the cycle progresses and then begins to increase until, for one hundred cycles, the resistance value remains below 34 Ω, which is much lower than that of the other electrodes, indicating that the composite electrode has excellent conductivity and stability. The micron-sized particles are not as agglomerated as the nanosized silicon particles, which effectively reduces the damage caused by volume expansion.

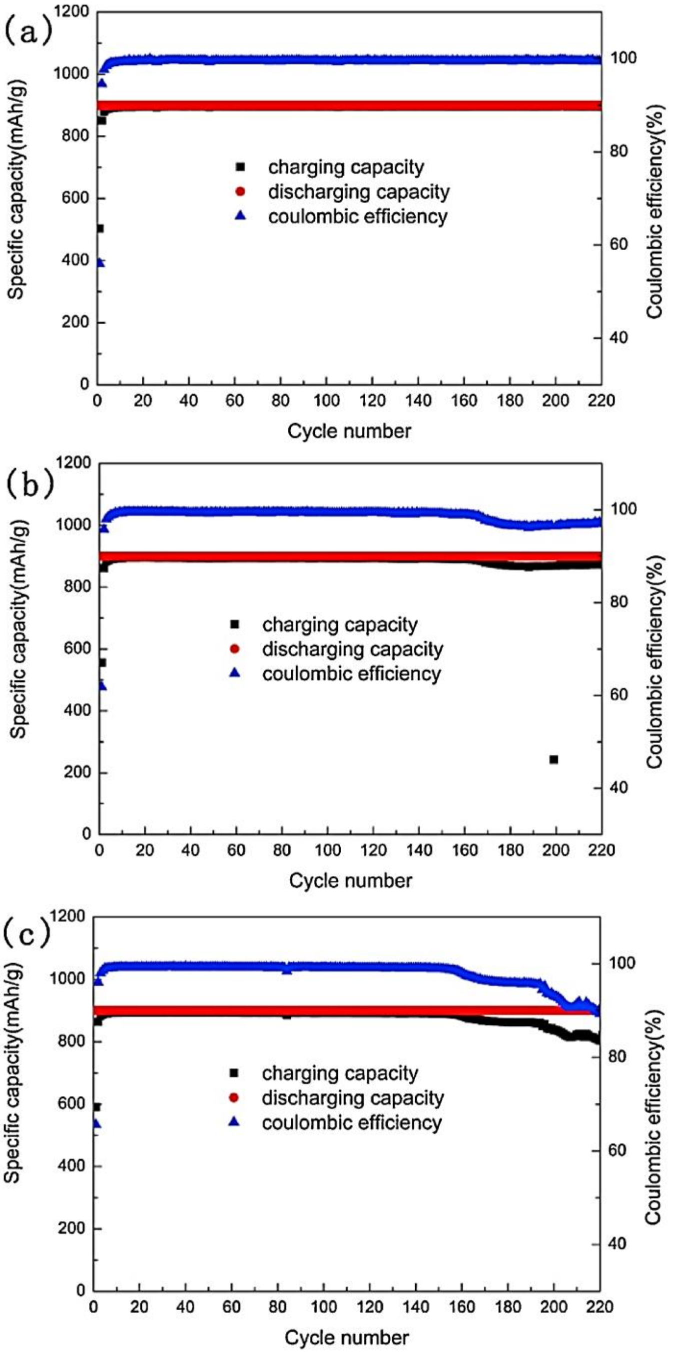

Fig. 1 Electrochemical studies of silicon with different dimensions [11]. (a) 1 mm. (b) 5.5 mm. (c) 13 mm.

Transition metal nitrides (TMNs) have received widespread attention because of their good electrical properties and mechanical properties. They have great potential to be an option in electrodes for lithium-ion batteries, such as vanadium nitride (VN) [12-14]. VN is directly synthesised by reduction or nitriding methods, where the large size of the prepared VN powder affects the performance of lithium-ion batteries. To research on the preparation of VN powders with a simple process and smaller size, a lot of efforts have been invested in the improvement of VN synthesis. Two VNs with different structures can be prepared by nitridation of vanadium-based precursors [15], which are presented as VN-O-V2C and V2CTz MXene. The VN-V2CTz MXene also displayed a nanolamellar microstructure exposing more electroactive sites compared to the lamellar VN-O-V2C. A large number of medium and large pores were present in the nitrided samples. These open pores are additional electrochemically active sites that can reversibly absorb and release lithium ions.

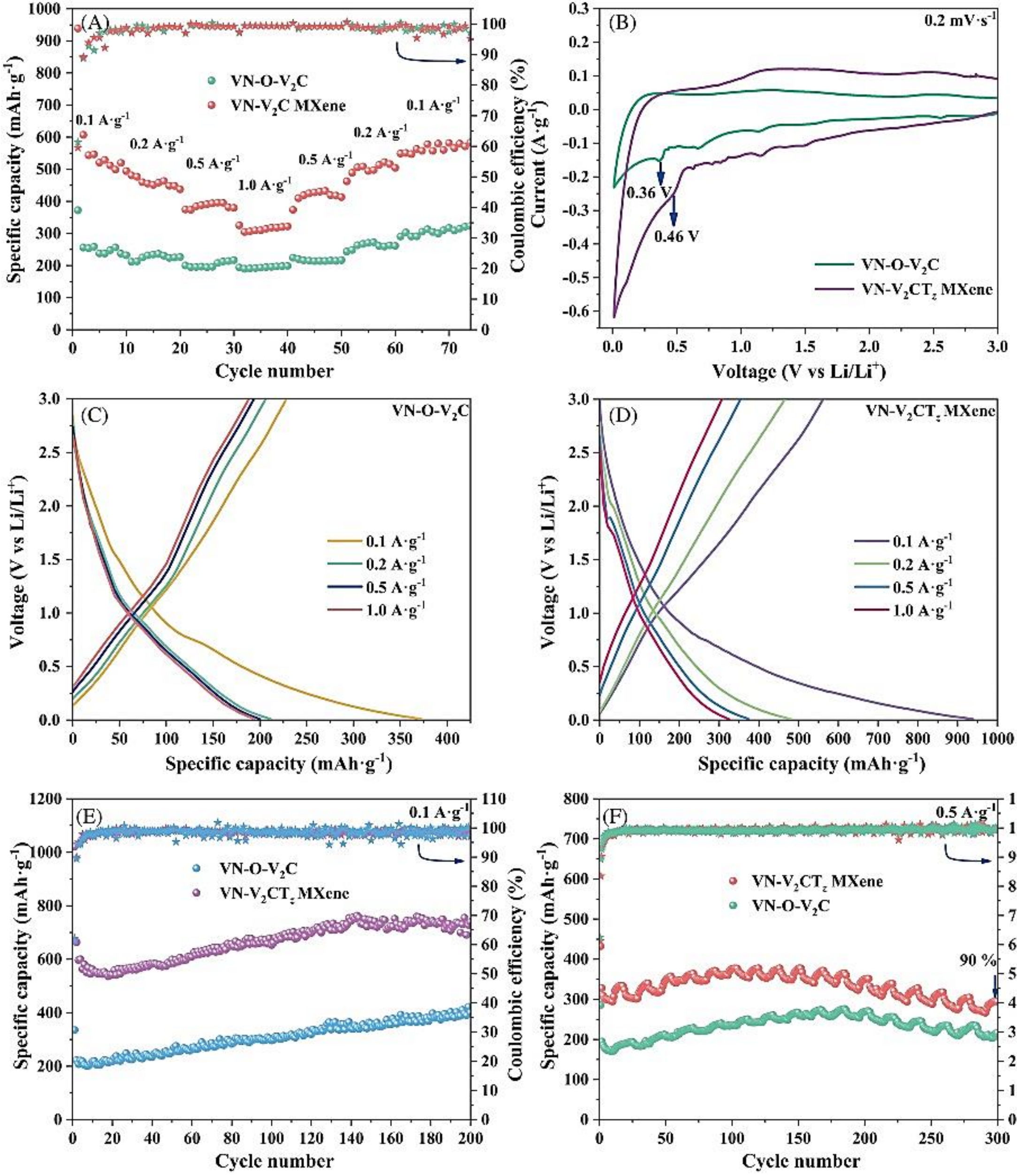

Fig. 2 The study of the electrochemical properties of two VNs [15]. (A) The rate capabilities. (B) CV curves. (C) and (D) Charge and discharge curves. (E) and (F) Cycling performance.

Fig. 2 shows the electrochemical performance of the prepared VNs. The two VNs for lithium-ion batteries show good electrochemical performance. The nanolamellar VN-V2CTz MXene performed better due to its unique nanolamellar structure, which is structurally supported by interlayer aluminium atoms, which promotes lithium-ion migration and builds a solid framework for lithium-ion insertion/degassing. Compared with VN-O-V2C, the capacity of VN-V2CTz MXene is more prominent, which is attributed to its unique nanolamellar structure. The larger specific surface area and more active sites are conducive to improving the permeability of the electrolyte and facilitating the diffusion of lithium ions into the layer. A large number of pores in the VN-V2CTz MXene laminate structure provides a number of active sites, which effectively reduces lithium ion losses and generates additional capacity in the form of pseudocapacitance. Although the Coulombic efficiencies were low in the initial state, 59.85% and 61.38%, respectively, they gradually increased to nearly 100% with cycling. The irreversible capacity loss might be related to the generation of solid electrolyte interphase (SEI) films. Two obvious irreversible cathodic peaks were found, which also proved that the formation of SEI films in the first discharge led to the initial coulombic efficiency decrease. They have excellent cycling ability, and the VN-V2CTz MXene showed a better level, and its reversible capacity reached 738.7 mAh/g after 200 cycles. With the cycling, the reversible capacity increased gradually. Meanwhile, sub-micron sized materials are beneficial in providing a larger electrode/electrolyte contact area, which significantly improves the electrochemical reaction kinetics. As the number of cycles increases, the edges between samples of small size also become areas where lithium ions can be stored.

3. Nanoscale garnet solid electrolyte-modified diaphragms for lithium metal batteries

Lithium metal batteries with lithium metal as the negative electrode are favoured by researchers because of their high theoretical capacity. However, there is a problem of lithium dendrite growth. The growth of lithium dendrites will puncture the diaphragm leading to an internal short circuit in the battery, triggering the battery combustion. Lithium dendrites growth will generate useless dead lithium, which consumes the electrode material. The growth of lithium dendrites generates useless dead lithium, consuming the electrode material and affecting its safety and stability.

Replacing lithium metal with lithium alloys as the anode material is a good choice because lithium metal doped with other substances produces fewer lithium dendrites. In addition to improving the electrode material, improving the SEI layer by adjusting the electrolyte can be used to achieve a better response to the electrode material [16]. But ultimately, liquid electrolytes can’t fundamentally solve the safety issues caused by lithium dendrite growth, so scientists are looking to non-flammable solid electrolytes with a high level of safety. Among them, lithium lanthanum zirconium tantalum oxide (LLZTO) can perform well both physically and electrochemically. In this section, a polyolefin-based diaphragm substrate dilute hybrid solid-liquid electrolyte coated with an LLZTO-coated film is highlighted.

Two problems were encountered during the preparation of the slurry. Due to the large size of the coarse LLZTO powder, it was impossible to achieve uniform dispersion. The slurry solidified and could not complete the coating. To this end, a ball milling process can be used to refine the particle size and prepare a porous composite film with excellent performance. The electrochemical properties are also highlighted in this experiment, as shown in Fig. 3. PE@LLZTO exhibits the best electrical properties. PE@LLZTO diaphragm has the smallest potential difference of only 71 mV, which is due to the creation of more ion transport channels in the presence of LLZTO and optimises the transport of lithium ions and reduces the effects of concentration differences as well as polarisation. The PE diaphragm with LLZTO added played an obvious guiding effect on lithium, greatly inhibiting the growth of lithium dendrites and making them flatly deposited on the electrode. The initial polarization voltage of the cells with ordinary PE diaphragm was very large, and as the time proceeded, there was a drastic increase in the polarization voltage, which led to the failure of the cells. Although the initial polarisation voltage also increased in PE@LLZTO, it reached a gradual smooth state with cycling and remained for more than 1000 h, which demonstrates the stability of this material as a battery electrolyte. PE@LLZTO has much smaller impedance both before and after reaction, which also demonstrates the material’s good stability.

The above data have proved that under the action of this diaphragm, there is a significant improvement in both stability and safety, which proves that the PE@LLZTO diaphragm has a high feasibility for practical application.

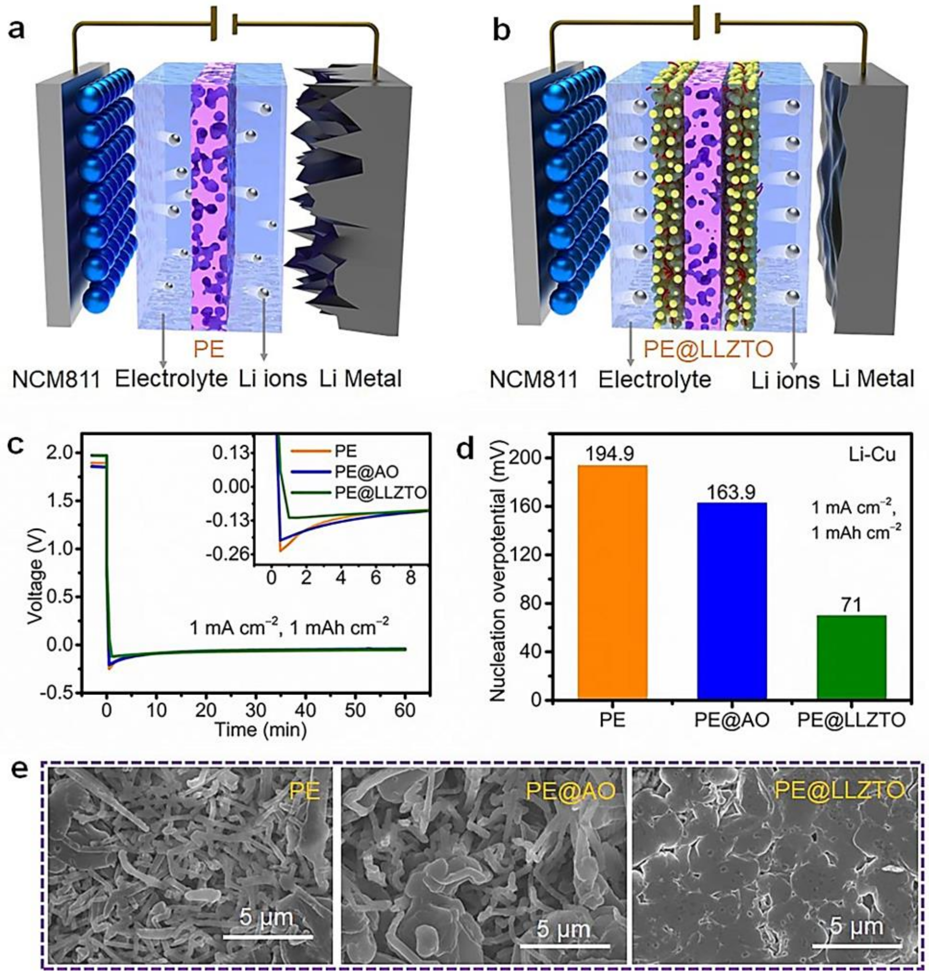

Fig. 3 The study of the effect on lithium deposition [16]. (a) and (b) Schematic illustration for the transportation of lithium ions. (c) Deposition voltage variation curves for different samples. (d) Nucleation overpotential for different samples. (e) SEM images for different samples.

4. Use of nano-In2O3 as a multifunctional filler for SPE in lithium-sulphur batteries

Lithium-sulphur batteries are widely regarded as an ideal battery system. However, in the current application scenarios, in addition to being affected by the lithium dendrite growth problem of conventional lithium batteries, lithium-sulfur batteries also suffer from the sulfur shuttle effect due to sulfide properties, limiting their large-scale applications. Researchers have mainly adopted different strategies, such as encapsulating sulfur in carbonaceous materials and blocking of polysulfide shuttling by improving the properties of electrolyte diaphragms with porosity. In addition, the growth of lithium dendrites as a result of a side reaction between the liquid electrolyte and lithium anode has also greatly affected the safety issue, and thus the idea of using a solid polymer electrolyte (SPE), which has good processing performance, elasticity to volume change and low interfacial impedance. However, the currently applied SPE prepared with poly ethylene oxide (PEO) has the shortcomings of high ionic conductivity and insufficient mechanical strength, which makes it unsuitable for electrolyte material and the mechanical strength is not enough to resist the growth of lithium dendrites. To address the problem, a nano multifunctional electrolyte based on PEO and containing nano-multifunctional nanocrystals will be introduced [17].

Compared to other contents, when the content is 12%, both mechanical and electrical properties perform better, and through theoretical analysis, these excellent properties are attributed to the nanostructured In_2O_3. When the content exceeds 12%, agglomeration occurs due to the high surface energy of the nanoparticles, leading to a decrease in the action. This material exhibits a lower polarisation voltage as well as a longer cycle life at different currents, suggesting that the alloy generated at the interface guides the deposition of lithium metal.

A lithium-indium alloy layer appeared on the surface of the lithium metal electrode, and the peak intensity of the alloy peak in the XRD increased with time, suggesting that the alloy layer was generated during the battery cycling process. The resulting alloy has a low reactivity, which avoids the reaction between lithium metal and the electrolyte. Moreover, the high intrinsic diffusion coefficient of the alloy promotes the migration of lithium metal and avoids the formation of lithium dendrites. Under the influence of the alloy layer, lithium deposition is flatter, effectively inhibiting the growth of dendrites. In a study of the shuttling effect by means of a permeation device, both experimental results and XPS showed that the material inhibited the migration of sulphides very well (Fig. 4). At a current density of 0.5 C, the pouch cells were able to provide a relatively stable capacity and operate normally without short-circuiting. In addition, the pouch cell can still provide stable current to light up the light bulb, which demonstrates that the PEO/LiTFSI/In_2O_3 SPE has excellent safety performance and practicality under extreme conditions.

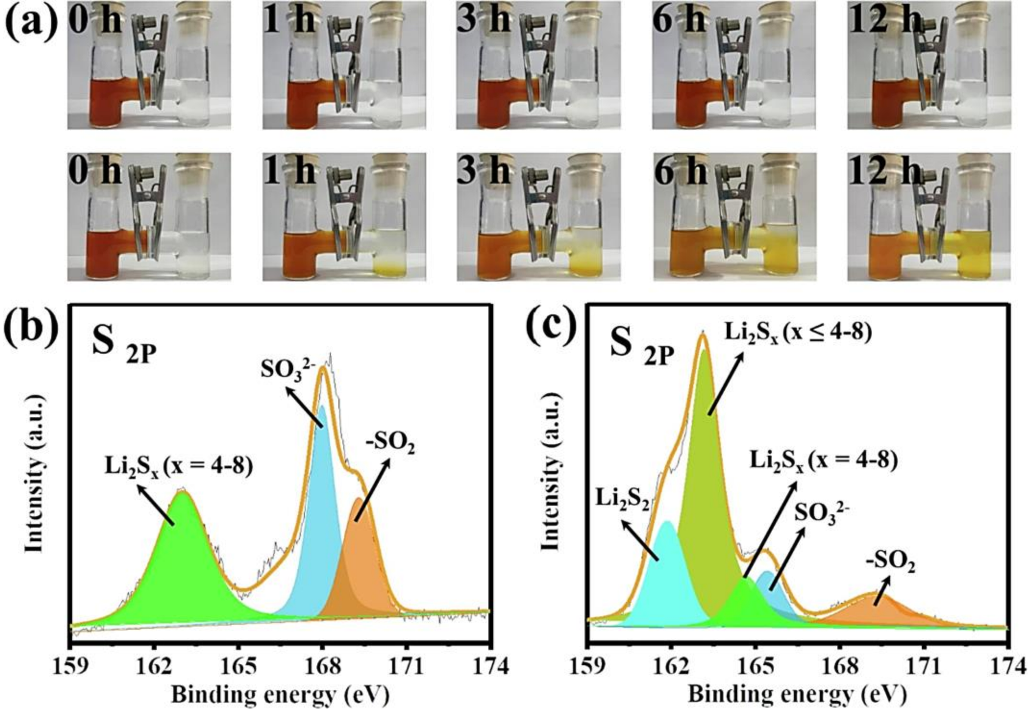

Fig. 4 A study of the sulphide shuttle effect [17]. (a) Permeation experiments for different samples. (b) and (C) XPS analysis.

5. Conclusion

The references of nanotechnology have been proven to solve several problems currently faced by lithium batteries, and this research focuses on the current status of research in recent years, as well as analysing and summarising some of the mechanisms that can enhance the electrochemical performance of the batteries. In the global large-scale research on lithium nano-battery, the addition of nanomaterials has significantly improved battery performance, such as adding multifunctional nano-fillers in solid-state electrolytes, replacing the anode of lithium-ion batteries with nano-layered VNs, and using nano-porous silicon as a better choice of anode for lithium-ion batteries. Lithium dendritic crystal growth has been solved, and the shuttling effect of polysulphides in lithium-sulphur batteries. In addition, various issues such as low safety of common liquid electrolytes, low ion conductivity of common solid electrolytes, and low reversible capacity of batteries have always needed to be addressed. This can also refer to the introduction of nanomaterials to help propose new solutions.

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