Progress in research on the performance and service life of batteries membrane of new energy automotive

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Batteries membrane materials are widely used in new energy automobiles such as hybrid vehicles, fuel cell vehicles, and pure electric vehicles. Membrane consists of two categories: fuel cell membrane (power unit) and power battery membrane (charge and discharge device). With rapid development of the processes and technology of cell membrane materials, there is urgent need to study their properties and service life. The article summarizes the recent research progress in proton exchange membrane materials, lithium battery separator materials, and nickel-hydrogen battery separator materials. Based on our laboratory research, the paper features the affecting factors and mitigation strategy of performance and service life for automotive battery membrane materials. Future direction for the batteries membrane material of new energy automotive is discussed.

new energy automotive, battery membrane material, performance, service life

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Energy shortages and air pollution are the primary challenges facing global automotive industry. The transport sector accounts for 52% in global oil consumption in 2010 [1]. The world retains about 800 million cars and the number will reach 1.2 billion by 2020. Transport sector's energy consumption has become the main source of pollution and greenhouse gas emissions, making energy transformation imperative. New energy is the clean energy to replace gas and diesel, with high efficiency, environment friendliness, and low emissions. Nickel-hydride, lithium battery, and fuel cell are the major clean energies to provide power and become highly efficient for new energy vehicles, including hybrid electric vehicle, battery only electric vehicle and fuel cell vehicle. Energy battery is green energy and independent from the bottleneck of oil productivity, attracting attentions from many governments, research institutions and enterprises for R&D [2,3]. Among new battery materials, mem-

brane materials work in a complex environment with high requirements for performance and are the first to degrade (even if other anode and cathode materials still work), becoming a weakness for battery system [4,5]. Membrane material properties determine the battery's thermal effects and resistance, directly affecting the battery performance and service life. Therefore, it is urgently needed to enhance the service performance and extend battery life. Taking proton exchange membrane materials, lithium battery separator materials, and nickel-hydride battery separator materials as examples, the paper introduces the research progress of membrane materials and discusses new methods to improve the performance and service life.

1 Proton exchange membrane material

Fuel cell is not a battery, but a power generator, where energy is stored in hydrogen and the chemical reaction

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between hydrogen and oxygen produces electricity. Compared with alkaline, phosphoric acid, molten carbonate, and solid oxide, proton exchange membrane (PEM) fuel cell features with high energy density, low operating temperature, quick start, long life, compact structure, light weight, non-corrosive, and free from the impact of carbon dioxide [6]. It has a large share in new energy fuel cell vehicles, as shown in Figure 1. If battery life can be effectively extended, the cost of vehicle can be reduced [7]. PEM stays in moist state, with one side exposing to air. Two sides are affected by voltage and the internal migration of protons and water [8]. It possesses the general properties of composite materials. After the electrochemical reaction, chemical energy can be turned into electricity. PEM provides channel for proton, lowers internal resistance and increases power output [9]. It enables proton to migrate through the membrane from anode to cathode and loop with electron in external circuit to provide electric current [10]. Therefore PEM directly impacts the performance and service life of fuel cell.

PEM is a thin-film polymer composite materials, and in essence, an electrochemical reaction generator. The mechanism is to turn chemical energy directly into electricity without combustion. The optimum operating temperature is 80–90°C, but room temperature also works [10].

The mechanism of PEM is shown in Figure 2. The structure of PEM makes PEM likely to degrade in chemical aspect, which lowers the performance and shortens the service life [11]. Degradation of the polymer is the lowering of polymerization degree under the effect of chemical or physical factors, resulting in an irregular breaking of macromolecular chains [12]. It transforms into substances with lower molecular weight, where link is removed from the end. Cross-linking reaction is to form macromolecular network structure from a number of linear polymer chains through the establishment of chemical bonds between the chains [13]. Degradation and cross-linking reactions often simultaneously occur in the degradation process, including changes in appearance, physical properties, mechanical properties and electrochemical properties [14].

Attenuation of PEM is affected by multiple factors. Under 0.4–0.7 V, H_2O_2 attenuates due to the lack of air. The electrolytic reduction of cathode catalyst is the main cause

Figure 1 Shares of various fuel cells.

Figure 2 PEM mechanism.

of attenuation. Thinner membrane has faster attenuation [15]. Before significant increase of hydrogen, the attenuation was low at first and then accelerated, with impedance unchanged significantly [16]. Mass spectrometry indicated that the cathode discharge contains HF, CO, H_2O_2 and CO_2 . Wu et al. [17] studied the relationship between humidity and the degradation of catalysts and found that the more humid the membrane electrode, the easier for Pt ions to enter the electrolyte, and the faster the loss of the catalyst. Variable loading cycle might crack the catalyst layer. Mei et al. [18] found that CO is absorbed on the Pt surface, affecting performance much more than large Pt particles. Karl et al. [19] tested the corrosion of catalyst on PEM and found that catalyst enters the electrolyte after the decomposition of carbon carrier. Yan et al. [20] suggested that impact of CO_2 is greater for small current and high potential. The impact reduces when current density increases, implying that pressure penetration is the cause of attenuation of PEM. Attila et al. [21] tested steady conditions versus dynamic conditions and found the attenuation rate to be hopping. PEM is affected by the harmful components in the air and filter can enhance the performance. Zhang et al. [22] tested PEM under open circuit voltage and regarded the attenuation of structural changes in the catalyst layer as the main reason. Platinum oxide and catalyst poisoning can be recovered partly by the voltage loop, but it cannot prevent the degradation of PEM. Hydrogen pump can be used to enlarge catalytic interface, applying voltage to turn CO to CO_2 to optimize PEM [23]. Activation for PEM can be achieved with 20 mA/cm^2 constant current or voltage cycle. Both methods require the similar length of time [24].

Erosion and thermal radiation are the main cause of damage in PEM [25]. Rapid degradation of PEM is due to

the formation of H_2O_2 by O_2 and H_2 under open circuit voltage which is strongly erosive [26]. On the Pt surface there are complexes that can be removed by cyclic voltammetry [27]. Using zirconia to decompose H_2O_2 can slow the PEM degradation [28], and alkali metal can improve the PEM stability [29]. PEM's resistance to puncture must be high to prevent thermal radiation damage [30]. Wet-dry cycle will damage membrane and the electrochemical surface area and high-frequency impedance can be used to estimate energy attenuation [31]. Dehydration will take place under 60°C , side chain of sulfonic acid resin breaks around 100°C , and pyrolysis starts at 280°C [32]. Long-term storage would lead to the degradation of PEM. Hot acid/water pre-processing can improve the humidification and extend service life, but will reduce the elasticity of PEM [33].

2 Lithium battery separator material

Lithium is the lightest metal element with a relative atomic mass of 6.94, having the minimum electrochemical equivalent $[0.26/(\text{Ah})]$ and the most negative standard electrode potential (-3.045). These characteristics make it ideal for electrode material [34]. In the lithium battery, separator is very important to isolate positive and negative poles to avoid short circuit and allow electrolyte ions pass. The principle is shown in Figure 3. Lithium-ion batteries require high strength separator which directly contacts with hard surfaces of poles. When crystal is formed, separator is easy to be penetrated [35]. Lithium penetration rate reflects the degradation of separator [36]. In new separator the rate is generally no more than $1 \text{ mA}/\text{cm}^2$, but in degraded separator the rate reaches $10\text{--}20 \text{ mA}/\text{cm}^2$ [37]. Open-circuit voltage reflects the penetration from anode to cathode and the voltage decreases significantly after the degradation of separator [38].

Optical interferometry experiment is used to test the evolution and penetration rate of lithium. The relationship between permeability and durability is non-linear. In the case of longer life, lithium penetration rate does not change over time [39]. Enhanced durability test shows open circuit voltage associates with separator degradation [40]. Lithium cobalt oxide (LiCoO_2) has stable electrochemical perfor-

mance with high reliability (Figure 4(a)). For high-current applications, large capacity long-life lithium-ion battery is structured, as shown in Figure 4(b). The thermal stress on high-current lithium-ion batteries has direct impact on the electrochemical performance. After multiple charge-discharge cycles, cracks may appear on the particle's surface [41,42]. The sharp interface between two-phase and high-intensity stress leads to cracks. Crack further causes electrode polarization and also weakens the contact between conductive additive and the collector, resulting in the loss of battery capacity.

LiCoPO_4 crystal structure shows that the direction of six oxygen atoms in three-dimensional stack improves the diffusion of Li^+ and high-current life [43,44]. In addition, multi-layer structure was proposed, as shown in Figure 5, to meet the charging characteristics for large capacity vehicles. Materials under $3.0\text{--}3.5 \text{ V}$ have a capacity of $1.1\text{--}1.4 \text{ Ah}$, and 3.8 V with 1.5 Ah [45].

Figure 4 Different structures for Li-Co battery. (a) LiCoO_2 structure; (b) large current structure.

Figure 3 Lithium battery.

Figure 5 Large capacity separator and battery material structure.

The tensile strength, elongation at break, and lateral shrinkage also have certain requirements. The separator stretched in different directions has varying intensity, leading to vertical contraction and contacts between electrodes under high temperature [46]. Therefore regulating separator structure should take into account the mechanical properties of microporous separator to get the best performance and service life.

Nanotechnology helps increase the contact area between electrode and electrolyte, greatly improving battery performance [47]. Cathode made from nano material has good features like uniformity, high crystallinity, small particle, and atom-level mixture [48]. When two fibers move against each other, the coated nanowire buckles the other nanowire to release charge to the fiber [49]. Experiments show that the electrode impedance becomes larger when water is lacked in the separator, resulting in material degradation. Carbon nanotube can also be used as separator. When there is too much water, increase temperature and air flow. When there is inadequate water, lower the temperature and reduce air flow. Therefore, carbon nanotube separator can achieve a capacity of 700 mAh/g, exceeding the theoretical capacity of graphite's 372 mAh/g. The capacity retention rate after 60 charge-discharge cycles is 65.3% [50]. Nanotechnology eases the lithium ion phase-change or volume change during charge-discharge process and maintains the stability of lattice structure, assuring performance with prolonged service life.

3 Ni-MH battery separator material

Thermal effect is one major cause of the degradation of nickel-hydrogen separator material. High temperature breaks the material strand and generates free radical molecules. Chain reaction leads to degradation and cross-linking of polymer materials. Changes in humidity will cause expansion and contraction of the separator. The pressure changes could accelerate rupture. When load changes, the lack of air may lead to abnormal reaction on both sides and accelerates the degradation. To compare the temperature damage with pure electrochemical polarization, oven method is used and it is found that micro-current has restoring effect [51]. The introduction of nanotechnology into Ni-MH battery can reduce the contact resistance between Ni particles to form a good conductive network, increasing the discharge current and improving stability. Energy storage alloy powder at nanoscale can reduce material costs by 10%–20%, achieving the capacity retention rate of 98% [52]. The material contains nanoscale crystal particles so that storage alloy has high electronic conductivity and solid-phase diffusion rate. By measuring attenuation under high current and considering micro-current recovery, it is found that performance relates with current strength [53]. Therefore the conservative method to reduce battery load can be extended.

Separator before and after charging under SEM mor-

phology is shown in Figure 6. The experiment tests material compositions [54] with different proportions. Sulfonation treatment can restrain the decomposition of separator and reduce self-discharge of the battery [55]. Discharge efficiency, high-current discharge performance and charge retention rate, can be used as new methods to examine the life cycle [56,57]. Nano-polymers have been used as separator materials. Under normal charge-discharge voltage range it stays in insulated state and only allows ionic conduction. When charging voltage reaches the control value, polymer is oxidized into electrically conductive state to form a short circuit inside the battery and protect from internal excitation [58]. The study of voltage-sensitive separator requires the establishment of correlation between macroscopic properties and microstructure of nano composites [59,60]. A representative model and stress distribution is shown in Figure 7.

For voltage-sensitive separator, metal, ceramic and polymer alternate in stacking arrangement to parallel with electrode layer. The polarization direction is perpendicular to the layer (Figure 7). Field equation along polarization direction is

Figure 6 Morphology of separator. (a) Before charging; (b) after charging.

Figure 7 Voltage-sensitive separator. (a) Model; (b) stress.

$$\bar{E} = fE_c + (1-f)E_p + (1-f)E_m, \quad (1)$$

where E_c , E_p and E_m represent the ceramic, polymer and metal state, variable with dash is the average value, and f the volume ratio of ceramic state. With boundary condition, from eq. (1) the average separator piezoelectric coefficient can be obtained directly:

$$\bar{d} = \frac{fd_mE_p + fd_pE_m + (1-f)d_cE_c}{fE_p + fE_m + (1-f)E_c}, \quad (2)$$

where E_c , E_p and E_m represent the ceramic, polymer and metal state piezoelectric coefficient, eq. (2) shows that even a thin layer of nanoscale separator may significantly reduce the effective piezoelectric coefficient.

4 Fuel battery pack

Compared with battery pack, single cell has a significantly shorter life and lower performance. In order to enlarge capacity, battery pack needs dozens or even hundreds of single cells. Single cell membrane and battery performance are equally important, considering their heating, resistance, and penetration properties. Batteries with membrane life of 7–10 years may be damaged after 3–5 years of use in the car [61]. Some even degrade in less than one year, which is unreliable and easy to cause accident. Power output varies frequently, causing battery to work in a highly dynamic process for long term. Consistency between single cell membrane is getting worse [62]. It is necessary to determine the exact state of single cell membrane for load balancing. The second is the design and control of the balancing system to moderate the non-uniformity [63]. Effective state estimation and identification of single membrane as well as design and control of balancing system will assure the life of pack. Temperature distributes unevenly in the battery pack and its impact on each single cell membrane is inconsistent. The performance difference will gradually increase and result in poor temperature cycle, leading to increased temperature difference and causing serious battery degradation and shortened life expectancy.

To improve consistency between single cells, microcontroller module can be used for direct control to realize dynamic equilibrium [64]. The structure is shown in Figure 8. Single cell membranes are connected to the jack stand. A step motor drives horizontal slider to move around. Different displacement corresponds to different cells. On the horizontal slider there are vertical sliders and rails. When the balance wire plugs into the corresponding jack of a cell, the circuit is enclosed. Such design has low cost, high reliability, and good scalability. Balancing system and battery capacity can be proportionally matched. The heating problem can be avoided because battery power only transfers between the membrane

Figure 8 Battery pack balancing.

stack and the balanced cell membrane. Charge and discharge is subject to the state of single membrane. The impedance can also be identified when the cell membrane works.

Study of balanced life of membrane pack shows that high-capacity battery material is significantly affected by the number of cycles [65]. After 500 cycles, the internal temperature differences at both ends of the battery pack are 15 and 19°C respectively. Using different cycles and speeds to intake the air, degradation of battery can be slowed and thus the battery life can be extended [66].

5 Conclusion and prospects

After testing a variety of operating conditions of chemical structure, the laws governing material properties can be determined. Construction of the microscopic structure of polymer materials is the basis for research. Molecular model shall be established on atom level to simulate the structure and analyze its static and dynamic behavior, such as adsorption, diffusion, and other processes. Studies on the life and degradation mechanisms in PEM, as shown in Figure 9, include the relationship between microstructure parameters and macroscopic mechanical properties, parameters expression of PEM cell, and material properties of cell membrane [67]. The maximum life of PEM can be approximated by the maximum permissible voltage change under rated current.

Batteries membrane material properties and service life is the current bottleneck for new energy automotive technology. Research of performance degradation and mitigation shall cover different temperatures and charge-discharge conditions to measure related parameters (temperature, resistance, and voltage). In addition to the research of large capacity cell, attention shall also be paid to the integration of membrane technology with battery systems and new energy vehicles. These are the key to the application of membrane materials, which also provides support for energy saving and environmental protection.

Figure 9 Framework of PEM analysis.

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