

A short review on electrode materials and processing of Lithium-ion battery

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Abstract

The purpose of this paper is to review the efficient electrode materials and process adopted for electrode fabrication (mainly cathode) of Lithium-ion Batteries (LIBs). This article discusses the high performance cost effective active materials for fabrication of cathode. The comparison and difficulties of both the processing methods using non-aqueous and aqueous medium has been discussed in terms of cost and environmental issue. In this article various aqueous formulations of cathode electrode slurry and their electrical properties as well as the electrochemical performance of LIBs are reported with the application of various water soluble binder and other additives.

Keywords: Additives, Adhesion, Cathode, Binder, Lithium-ion Batteries.

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1. Introduction

The present fossil fuel based energy economy is at a serious risk due to several factors, including the continuous increase in the demand for oil, the depletion of non-renewable resources and the dependency on imported crude oil. Another worrying aspect of the present fossil fuel energy economy is associated with CO₂ emissions, which is increasing at a constant rate, resulting in global warming with associated series of dramatic climate changes. Therefore, the urgency for energy renewal requires the use of clean energy sources. The CO₂ issue, and consequent air pollution in large urban areas, may be only solved by replacing internal combustion engine (ICE) cars with zero emission vehicles, i.e. electric vehicles (EVs) or, at least, by controlled emission vehicles, i.e. hybrid electric vehicles (HEVs) and/or plug-in electric vehicles (PHEVs). Accordingly, investments for the exploitation of renewable energy resources are increasing worldwide, with particular attention to wind and solar power energy plants, which are the most mature technologies. The intermittence of these resources requires high efficiency energy storage systems. Electrochemical systems, such as batteries, that can efficiently store and deliver energy on demand in stand-alone power plants, as well as provide power quality and load levelling of the electrical grid in integrated systems, are playing a crucial role in this field. Indeed, in virtue of their high value of energy efficiency, lithium batteries are expected to provide an energy return factor higher than that assured by conventional batteries, e.g. lead-acid batteries [1]. Lithium battery is characterized by high specific energy density, high power density and long life. Since the first commercialization of secondary lithium ion battery in the 1990s, it has been used as one of the most important safe power sources for various energy storage applications in portable electronic devices such as cellular phones, laptop computers, cameras and other modern-life appliances as well as for sustainable electrical vehicles, such as HEVs and EVs [2 - 8] because of its high energy density, relatively good safety, and good cycling stability. LIBs are produced in the order of billions of units per year. However, scaling up the chemistry of common lithium ion batteries for these applications is still problematic. Barriers of various natures including safety, costs, wide operational temperature range and materials availability, still prevent the large scale diffusions of lithium ion batteries for renewable energy plants and electrical vehicle applications. Several countries, including Japan, United States and Europe, are allocating large investments to support R&D programs aimed to solve these problems and thus promote the development of advanced, efficient lithium batteries [9].

Generally, the performance of any device directly depends on the materials on which it is formed; this is true for lithium batteries. The LIB is manufactured through a series of processes, namely, electrode preparation, cell assembly, grading and formation, performance evaluation and safety evaluation. Now, with the help of recent research activities, many details of the technology are established, i.e., from material selection, synthesis, structure, doping through production processes to quality control of electrochemical features of secondary lithium-ion battery.[10 - 12] The performance in terms of energy, power and life issues of lithium ion batteries are closely related to material and interfacial ones. Basically, the performance of a battery relies on the

internal configuration and internal structures of the constituents. However, relevant studies of these phenomena are few. [13 - 16]. Although a commercial success, lithium ion batteries are still the object of intense research mainly aimed to the fabrication and characterization of improved electrode. The application to electric vehicles and grid energy storage is limited by performance and cost [17].

The main components of battery costs are materials, labour, and overhead with the cost of materials and associated process making up over 80% of total costs of high power batteries [18]. Thus, the key to reducing costs of LIBs lies in achieving low cost materials and developing low cost material processing [12] which is especially true for the cathode. Cathode materials and processing represent the majority of the total cost of high power batteries [2]. For preparation of composite electrode, active materials, conductive additives, and polymeric binders are generally blended into a solvent through multiple mixing with a mixer and then the slurry is coated on current collector [11, 19]. According to the type of solvent used, the processing of electrodes can be classified into two categories: water-based (aqueous) and organic solvent-based (non-aqueous) systems. As the voltage of the lithium ion batteries is much higher than that of electrolysis of water, any water must be removed from the electrode material. Below 10-20 ppm of water is considerable, which led the industry to focus on non-aqueous approach for processing of electrode. But considering the cost, safety and environment aspects, recently more efforts have been focused on research to identify the suitable alternative binders and additives for aqueous processing. However, transition from non-aqueous system to aqueous one introduces some unexpected difficulties, due to different polarities of the solvents and surface chemistry of solid components, such as particle agglomeration, slurry stability, dispersion of particles, viscosity control, wetting of the slurry to the current collector, and adhesion between slurry and current collector. Recently, many reports have demonstrated that the electrochemical performance of a battery is affected by the variables such as electrode ingredients, electrode fabrication process, processing conditions, and dispersion and distribution of particles [15, 16, 20 - 23]. In addition to the effects of material selection, the processing methods also affect LIB performance and thus, are worthy of examination. In this regards, aqueous processing for electrode slurry formulation is challenging in the present scenario.

2. Transition from non-aqueous to aqueous process for electrode fabrication

It is well-known that in the preparation of electrode for LIBs, layered lithium transition metal oxides (LiMO_2 , $M = \text{Co, Ni, Mn}$) such as LiCoO_2 , LiFePO_4 , LiMn_2O_4 and LiNiO_2 are most widely used category of cathode active materials and carbon or graphite are anode active materials. However, in general LiMO_2 suffers from safety concerns and structural instability and cannot support high energy Li-ion batteries [24]. In this respect, lithium metal phosphates LiMPO_4 ($M = \text{transition metal}$) have been regarded as promising cathode materials for applications in rechargeable Li-ion batteries. Since first introduced by Goodenough in 1997, LiFePO_4 has been considered to be the most promising alternative to LiMO_2 for the next generation lithium-ion batteries, due to its low cost, excellent cycle stability [25, 26], high discharge potential (around 3.4 V versus Li/Li^+), good thermal stability [27], environmentally benign and safe in nature. LiFePO_4 displays high stability of the capacity (170 mAh/g) during charge/discharge cycle. Because of these characteristics, it is considered as a very attractive candidate for the development of greener and cheaper batteries compared to LiCoO_2 and LiMn_2O_4 . Among the above materials, LiCoO_2 is also the most widely commercially used material because of the advantages of high operating voltage, high specific capacity, and long cycle life. However, high cost, poor thermal stability at elevated temperature, toxicity of LiCoO_2 makes it an unsuitable material for large scale application. Nevertheless, LiFePO_4 has poor electronic conductivity ($10^{-9} \text{ S cm}^{-1}$) and the low diffusion of Li^+ ion in an electrode [28, 29] which results in losses in capacity and rate capability and thus hinders the commercial application of LiFePO_4 . To enhance the electronic conductivity, the commonly used approach is the surface coating of LiFePO_4 with a conductive material such as carbon [30, 31]. Using fine particles of LiFePO_4 has been suggested as an effective strategy for the improvement of the diffusion of Li^+ [32, 33] and good electrochemical properties, but the agglomeration of fine particles during the process of electrodes is a future problem and should be considered. Usually, the active material (AM) is mixed with a fine carbon powder as conductive agent and an inactive polymer binder to enhance the adhesion of particles. For conventional lithium-ion batteries, the manufacturing process of LiFePO_4 cathodes involves a slurry processing in which LiFePO_4 is mixed with other additives in a solvent. So far, most of the research and the development in composite cathodes, as well as for those based on LiFePO_4 , have been focused on the use of fluorinated binder Polyvinylidene fluoride (PVDF)

and N-methyl-2-pyrrolidone (NMP) as the typical binder and solvent, respectively for all commercial lithium-ion batteries. Despite the widespread use of NMP, it has some disadvantages such as high cost, toxic, environmental issue associated with NMP recovery and not easily disposable at the end of the battery life [34, 35, 36]. Also it produces flammable vapors during electrode manufacturing, which requires expensive explosion proof processing equipment. On the other hand, PVDF has strong binding strength, but low flexibility. The low flexibility of PVDF can easily deteriorate cycle life characteristics of the battery due to breaking of the bond between active materials and carbon material and consequently expansion/contraction process occurs during charging and discharging [37] process. Therefore, in order to absorb the expansion and contraction stresses of the active material during charging and discharging, it has been suggested to adopt a binder having elasticity. Moreover, PVDF is costly (industrial cost in the multiton scale is around 15–18 EUR/kg). All these add up cost in both raw materials and processing of batteries. A new trend is now being developed to substitute the PVDF binder with alternative binders in the anode [38] that are less costly and more environmental friendly. Consequently, many efforts were focused on research to identify suitable alternative non-fluorinated binders. Some of the binders including polyimide [39] and silica-based gel [40], were suggested. Unfortunately, most of these binders are soluble in organic solvent which is dangerous to humans and the environment. Thus, the switch from non-aqueous to aqueous systems is vital. Considering cost and safety aspects of battery, aqueous binders have gradually replaced PVDF binder for the anode material. SBR/CMC composite agent is generally used as the aqueous binder; styrene-butadiene rubber (SBR) is the primary binder and sodium carboxymethyl cellulose (CMC) is the thickening/ setting agent. In previous years, several researchers widely applied aqueous binder in the anodes for Li-ion cells. Recently, attempts have been adopted on the use of aqueous system for the preparation of cathode slurry [19, 41- 43] since this approach poses less environmental hazard and lower in cost. In aqueous system, expensive NMP (>\$2.25/L when purchased in large quantity) is replaced with deionized water (\$0.015/L) and some water based binder (example: CMC binder; cost: 1–2 EUR kg⁻¹) substitutes PVDF binder (cost: 15–18 EUR kg⁻¹) [35]. As a result, the cost would be significantly reduced, and additionally, the process for recovery and treatment of NMP would be eliminated. A recent report on processing cost study in Oak Ridge National Laboratory (ORNL) concluded that this approach has a potential to save up to 70% in the electrode processing steps [44]. Consequently, there is the growing interest to fabricate the composite cathode through aqueous system.

3. Limitation of aqueous system

In contrast to non-aqueous processing, most of the recent work for fabrication of cathode relies on aqueous system considering cost and safety aspects. However, aqueous process creates some unexpected difficulties related to slurry formulation and stability. This process suffers from powder agglomeration which is ascribed to strong hydrogen bonding and electrostatic force introduced by the use of water as a solvent [45]. Therefore, the key issue in implementing aqueous system is to control the agglomeration so that dispersion of particles and stability of slurry can be improved.

Basically, particles agglomeration which affects significantly the slurry stability and viscosity control is caused by the interactions between colloidal particles. These interactions involve attractive and repulsive potentials, generated from Vander Waals and Coulomb forces, respectively. The net potential generated between Vander Waals forces determines the stability of the particles. Therefore, to minimize agglomeration, the key is to increase the repulsive potential (i.e., increase the Coulomb force) between particles which is mostly dependent on the particle surface charge as well as surface chemistry of colloidal particles [46]. The agglomeration can be eliminated by adding a dispersant to the aqueous slurry and the advances in this area are urgently needed.

The introduction of aqueous processing for the electrode preparation is limited by the stability of active material in water. If the active materials do not show satisfactory stability in water, during the preparation process its structure could be modified with a negative effect on the performance of the electrode. Carbon-coated LiFePO₄ performance is known to suffer from humidity absorption that leads to the formation of LiOH and the oxidation of Fe from the bivalent to the trivalent state. On the other hand, as the voltage of lithium-ion batteries is much higher than the voltage at which water electrolyzes, any water must be removed from the electrode material. Considering these facts, processing of electrode in aqueous environment obviously presents the risk of losing some capacity as the presence of ppm level of water can deteriorate the overall cell

performance. For this reason, the great attention should be taken on the optimization of drying condition of electrode sheet.

In aqueous system, it is essential to obtain a stable and uniformly dispersed suspension. But due to hydrophobic nature of carbon black, which is one of the major components in cathode formulation slurry as conductive additive, appears to have encountered difficulty to disperse in aqueous phase. To this end, additional additives, such as binders and dispersants, are required. Additionally, extra pretreatments, including physical and chemical methods, are required to disperse carbon material in aqueous systems. Physical methods include ultrasonication, ball milling, grinding, and high-speed shear mixing [47, 48]. Chemical methods include using chemical functionalization [49] or surfactants [50], refluxing carbon materials in concentrated acids [51], and oxidation of carbon materials using H_2O_2 [19]. Reducing the surface energy of the carbon particles with the addition of surfactants can improve their wetting or adhesion characteristics and decrease agglomeration effectively. Introduction of hydrophilic groups on carbon oxidation by H_2O_2 such as hydroxyls or carboxyls can enhance their dispersion in aqueous medium [52]. On the other hand, poor wettability of aqueous slurry on current collector and adhesion between the slurry and current collector is caused by the high surface tension of the dispersions in aqueous system induced from higher surface tension of water. This issue can be resolved by either lowering the surface tension of dispersions or enhancing the surface energy of current collectors. The use of a co-solvent or multi-solvent system like ethanol–water decreases surface tension of aqueous slurry. On contrary, the surface energy of current collectors can be enhanced by some heat treatment, such as corona discharge treatment (CDT) or plasma treatment. Recently, research at Oak Ridge National Laboratory (ORNL) has demonstrated these treatments and reported the improvement in wetting of the dispersion to the Al foil by decreasing the contact angle between $LiFePO_4$ aqueous suspension and Al foil from 41.8° to 0° via corona treatment on the Al foil [53]. But the relevant studies are less. Accordingly, innovative research efforts have been directed towards the difficulties of aqueous system that need to be overcome.

4. Present progress of aqueous processing

The positive or negative electrode of a lithium-ion battery (LIB) is actually a composite material that needs to carry efficiently the ionic reactants and the electrons to the surface of the electrochemically AM particles. This composite material needs to have mixed conductivity with both Li^+ ionic and electronic conductivity. Such composite electrode is generally obtained by mixing together the AM grains with non-electroactive additives such as very fine powder of electronically conductive carbon and a binder material coated and calendered onto Al current collector. Binder has to be chemically and electrochemically stable in the operating potential window. As an inactive material to bind together the active material, the conducting agent and the current collector, the binder material is one of the crucial electrode components for improved electrochemical performance of electrode, such as cycle life in Li-ion batteries. The binder additive is in fact a mixture of several polymers and organic additives that combine critical multiple roles, has been discussed in this article. The major roles that the polymeric binder plays: (i) in the dispersion process and stabilization of the AM and C powders in the electrode slurry during the composite electrode preparation, and thus on the architecture of the electrode; (ii) in obtaining proper rheological properties to the electrode slurry with respect to the tape casting process. (iii) in the electronic and ionic conductivity of the composite electrode; and (iv) in the mechanical properties, i.e., the cohesion of the electrode and its adhesion with the current collector. Furthermore, from the viewpoint of energy density, it is desirable that all these requirements are achieved with a minimum amount of binder. Beyond its chemical and electrochemical stability in electrode/electrolyte interactions, the binder has to survive the large repeated dimensional changes of the electrode during the cycling of the cell. Because the surface chemistry and morphology of electrode materials vary, optimization of the binder system for different electrode materials is part of the routine in the development of high performance batteries. Basically, in the electrode manufacturing process through aqueous system, the electrode slurry consists of AM, carbon black and binder in water as solvent. The aqueous binders have been widely applied in the anodes for Li-ion cells over the years and are now examined for cathode. The example of water based binders are gelatine [54, 55], poly (acrylamide-co-diallyldimethyl-ammonium chloride) (AMAC) [37], poly acrylic acid (PAA) [56, 57], poly (vinyl alcohol) (PVA) [58], and CMC [59, 60]. In general, these materials are stiff and brittle, consequently leading to cracked layers that can delaminate from the current collector either during cell fabrication or cell cycling. Therefore, an additional rubber such as styrene-butadiene rubber (SBR) has been used to improve the overall cohesion of the

electrode, although the rubber does not contribute toward the dispersion efficiency of cathode slurries [61] and has a negative impact on the conductivity of the electrode [39]. In all cases, these water-soluble binders are not electrochemically active and their presence serves as impedance to lithium ionic conduction, especially at the active material interface [62]. The breakthrough in the area of aqueous processing of cathode has been achieved by the development of novel water-soluble binder (WSB). Presently, worldwide research efforts have been made towards the search for alternative binders. The identification of alternative WSB and dispersant is an important step in aqueous process. Several formulations of cathode are discussed in this article.

Table 1: Formulations of various aqueous cathode dispersions.

Authors	Cathode composition	Comments
Lee et al. [63]	LiCoO ₂ /graphite KS6/(PA/SBR+SCMC/SBR+PA/PBA+PA)(3:7)	Better dispersion quality of LiCoO ₂ , improvement of adhesion strength, improvement of rate capabilities and cycling stability significantly compared to PVDF and other WSB reported.
Tran et al. [64]	Li ₄ Ti ₅ O ₁₂ /super P CB/(PEGMA-co-MMA-co-IBVE)/LiTFSI	Coordination of the binder with lithium salt is necessary for the electrode to function, continuously cycle for a much longer period, higher capacity retention.
Lee et al. [19]	LiCoO ₂ /H ₂ O ₂ -VGCF-KS6/SBR/SCMC	Better dispersion of H ₂ O ₂ -treated VGCFs in cathode, improvement of electrical conductivity and C-rate capability of electrode.
Li et al. [65]	LiCoO ₂ /KS6/SBR/SCMC	More uniform binder distribution in electrode sheet, less electrical resistance, good adhesion strength and better electrochemical performance than organic based binder electrode.
Guerfi et al. [37]	LiFePO ₄ /CB/WSB/CMC	Cathode shows high flexibility with good adhesion, lower irreversible capacity loss and comparable cycle life to that with PVDF-based cathode.
Lee et al. [66]	LiFePO ₄ /CB/WSB-CMC/PAA	Incorporation of PAA significantly decreases the apparent viscosity of LiFePO ₄ pest and shifts the particle size distribution to lower value resulting an improvement of LiFePO ₄ dispersion properties. The electrode with PAA exhibited a specific discharge capacity (above 70 mAhg ⁻¹) about 7 times higher than that without PAA (10 mAhg ⁻¹) at high C-rate at 20 °C.
Li et al. [67]	LiCoO ₂ /KS6/PA-LA132/PAA-NH ₄	Addition of dispersant PAA-NH ₄ avoids the LiCoO ₂ powder agglomeration and binder accumulation around the powder. Improvement of electronic conduction and C-rate performance by the addition of PAA-NH ₄ 0.01 wt % and is not detrimental to its electrochemical performance.

Li et al. [68]	Li[Li _{0.2} Mn _{0.56} Ni _{0.16} Co _{0.08}]O ₂ /super P CB/CMC	This combination of electrodes have better structural stability during the electrochemical processes than PVDF-based electrodes, resulting improved cycling stability as well as very promising rate capability.
Li et al. [69]	LiFePO ₄ /super P C45/XG/PEI	Addition of PEI to aqueous LiFePO ₄ nanoparticle suspensions improves stability and reduces agglomerate size, dispersing LiFePO ₄ prior to CB when making final multicomponent suspension is beneficial for higher discharge capacity.
Tran et al. [70]	LiCoO ₂ /CB/(PEGMA-co-MMA-co-IBVE)/ LiTFSI	Optimized cathode (PEG based binder coordinated with LiTFSI) exhibited better cycle stability, higher rate capability, high specific area capacity.
Fongy Et al. [71]	Li ₄ Ti ₅ O ₁₂ /CB/NBR/CMC /TX-100	Despite the resulting poor electrode homogeneity, fairly good electrochemical performance could be achieved with this formulation, highlighting that the presumably low electronic conductivity of AM is not limiting, at least when AM are submicronic. Better rate performance is displayed for the electrode prepared without NBR.
Kim et al. [72]	LiFePO ₄ /super P CB/CMC	Electrodes display a specific capacity of about 160 mAhg ⁻¹ stable for more than 240 cycles.
Li et al. [73]	LiFePO ₄ /graphite KS6+CB /PBA/SCMC/PSSA	Addition of optima [PSSA] (2 wt%) improves dispersion homogeneity of LiFePO ₄ cathode, exhibits good cyclability and higher discharge capacity. Excess addition of PSSA is detrimental to the electronic conduction and energy capacity of cell.
Orlenius et al. [34]	LiFePO ₄ /CB/SBR	LiFePO ₄ (freeze granulation)/ SBR cathode exhibits very good capacity retention, PVDF-based electrode showed slightly better reversibility than the SBR-based one.
Chong et al. [74]	LiFePO ₄ / CB(AB) / PAALi /SBR	Cell with optimized PAALi /SBR based cathode exhibits good cycle life and improved capacity retention over traditional PVDF based cathode.

Lee et al. [75]	LiFePO ₄ /CB/CMC/PAA	Addition of PAA enhances dispersion properties of LiFePO ₄ , more compact and uniform microstructure of cathode. Cell fabricated with CMC/PAA potentially have much improved specific discharge capacity than that of CMC alone.
Cai et al. [56]	LiFePO ₄ /CB/PAA	Electrode shows better reversibility, lower resistances of SEI on LiFePO ₄ and charge transfer step, higher discharge capacity, better cyclic stability than that of NMP electrode.
Li et al. [76]	LiFePO ₄ /graphite KS6+CB /SBR/SCMC	Electrode displays good charge/discharge cyclability, much better capacity retention of 90% for sequential mixing of SCMC/SBR than that of 25% by the electrode with simultaneous mixing after the 100-cycles test.
Sun et al. [77]	LiFePO ₄ /CB/ C-CTS/SBR(2:3 wt)	Electrode with C-CTS exhibited comparable cycling capability with that with PVDF and CMC, but better high-rate performances both at room temperature and elevated temperature (60°C).
Porcher et al. [78]	LiFePO ₄ /CB/PVA-PEG /(CMC/HPMC)	Poorer discharge capacity at all rates is obtained with HPMC, while CMC-based electrode shows identical performance to PVdF-based electrode.
Porcher et al. [43]	LiFePO ₄ /CB/(PVA-PEG/ NBR) /(CMC/HPMC) / (SDS/ TX-100/CTAB)	More homogeneous CB distribution within composite electrode results better electronic wiring of the active material particles, leading to higher discharge capacity at high rate.

5. Conclusion

After detailed reviewing on the cathode materials and aqueous process for cathode manufacturing, it can be clearly concluded that most efforts have been conducted on LiFePO₄ and LiCoO₂ active materials and the use of other active materials such as, Li₄Ti₅O₁₂ or Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.08}]O₂ or other layered oxides are very little. Among all the cathode formulations studied, it has been observed that the improvement of dispersion and suspension stability of active materials and conductive additive in aqueous processes is due to the inclusion of various additives such as CMC (thickener), PEI, PAA-NH₄, PSSA, Triton X-100 (surfactant). Most of these additives with elastomeric binders produce good quality electrodes with homogeneous distribution of particles on the surface and improve adhesion strength, electrical conductivity, electrochemical performances, in terms of long cycle life, higher capacity retention and better rate capability compared to conventional PVDF/ NMP based electrodes. It is accepted that SCMC or CMC acts as an efficient thickener. Much attention needs to be focused on this area.

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