Review

Materials processing for lithium-ion batteries

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A B S T R A C T

Extensive efforts have been undertaken to develop and optimize new materials for lithium-ion batteries to address power and energy demands of mobile electronics and electric vehicles. However, the introduction of large-format lithium-ion batteries is hampered by high cost, safety concerns, and deficiencies in energy density and calendar life. Advanced materials-processing techniques can contribute solutions to such issues. From that perspective, this work summarizes the materials-processing techniques used to fabricate the cathodes, anodes, and separators used in lithium-ion batteries.

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1. Introduction

Since the early 1990s, when Sony manufactured the first commercial lithium-ion battery [1], extensive efforts have been undertaken to improve battery performance. Research and development has focused on two general areas: electrochemistry and materials processing. This paper summarizes the materials-processing techniques applied to the fabrication of lithium-ion batteries and their components and the issues associated with those techniques.

Numerous processing methods have been developed for lithium-ion battery fabrication and assembly. Processing research and development intended to improve performance can also affect the cost of fabrication. In 2000, the cost (labor and overhead) for a 18,650 cell was estimated to be $0.42 [2] (based on the assumptions of 76–104 people working on two lines in two shifts to produce 100,000 units of cylindrical cells per year [3]). This cost is about a factor of 3 higher than the target set by the US Department of Energy (DOE) to ensure deep market penetration by hybrid-electric and all-electric vehicles [4]. In order to reduce the cost of lithium-ion batteries to the desired target, it will be necessary to improve materials processing and to introduce thorough quality control measures in the manufacturing process, as has occurred in other industries, such as semiconductor production.

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2. Processing for electrolytes

An electrolyte for lithium-ion batteries should be able to dissolve and dissociate into the solvent system, and the Li ions should be able to diffuse in the system with high mobility. Conventional electrolytes consist of lithium salts dissolved in organic solvents [5]. Propylene carbonate (PC) has attracted attention [6,7] due to its high dielectric constant, the wide temperature range of its liquid phase, and its compatibility with lithium [6]. However, a solid electrolyte interface (SEI) film cannot be formed on PC-based electrolytes because the PC tends to intercalate with lithium ions into the graphite anode, resulting in continuous decomposition and severe exfoliation of graphite layers [1,8] and a large irreversible capacity loss during the initial cycling [9,10]. Many attempts have been made to improve the compatibility of PC with graphite by introducing additives, such as vinylene carbonate [11], butyl methyl carbonate [12], or triethyl orthoformate to the electrolytes [13]. The additives form an SEI layer at potentials higher than 1 V vs. (Li/Li$^+$) before PC begins to decompose [14]. In contrast, ethylene carbonate (EC) forms a stable SEI film on the surface of graphite and has been widely used in commercial solvents because of its good electrochemical stability, low cost, and high dielectric constant. These characteristics permit better ionic dissociation of the salt and improve ionic conductivity [15]. The high melting point of EC (~36 °C) precludes its use as an ambient temperature electrolyte solvent. Consequently, extensive efforts using different cosolvents, including PC [9,10], diethoxyethane [10,16], tertahydrofuran (THF), 2-Me-THF [17,18], and dimethoxyethane [19,20] have been made to optimize electrolyte composition. However, because these ethers can be oxidized by the charged cathode [10,16], they are not good EC cosolvents and do not meet electrolyte safety requirements. Linear carbonates, such as dimethyl carbonate (DMC) [21–25] or ethyl methyl carbonate (EMC) [26], commonly known as thinning solvents, are also used with EC to reduce its viscosity. This mixture has wide electrochemical stability and remains stable on a cathode surface up to 5.0 V [6]. Each component in a mixture of EC, DMC, and EMC has merits that are integrated into the mixture (e.g., the high anodic stability of EC on cathode surfaces, the high solvation of EC toward lithium salts, and the low viscosity of DMC/EMC to promote ion transport). This formulation represents the state of the art in lithium-ion electrolytes and has been adopted by researchers and manufacturers [6,19,27–30]. Other linear carbonates, such as diethylene carbonate (DEC) [31–34] and propylmethyl carbonate [35], have been investigated, but they show no significant improvement in electrochemical performance compared with DMC/EMC.

When considering electrolyte salts, LiClO$_4$ remains stable up to 5.1 V and has high conductivity in EC/DMC (9.0 mS cm^{-1} at 20 °C) [22]. There is less concern about metal dissolution from cathode materials because of the absence of fluorine species. Lower impedance has been reported for SEI films formed on anode surfaces in LiClO$_4$ electrolyte than for films formed in LiPF$_6$ or lithium tetrafluoroborate (LiBF$_4$) [36]. However, LiClO$_4$ is a strong oxidant and reacts easily with other organics because of the high oxidation state of chlorine, and thus raises safety concerns [37]. LiBF$_4$ remains stable up to about 5 V vs. (Li/Li$^+$) [38], but its application is limited by the low conductivity in EC/DMC (4.9 mS cm^{-1} at 20 °C) [5]. The preferred salt has been LiPF$_6$ because of its rapid dissolution in carbonate solvents and its low cost. The typical concentration of LiPF$_6$ salt is 1 M in an electrolyte system. Most liquid electrolytes composed of EC, DMC or EMC, and LiPF$_6$ are suitable for use in practical cells because they exhibit a conductivity higher than 10^{-3} S cm^{-1} at room temperature [22]. However, the flammability of these solvents and their vapors can cause a major safety issue in lithium-ion batteries.

Safety concerns have limited the full utilization of lithium-ion batteries. Extensive efforts have been made to formulate an electrolyte that is nonflammable and still works well. It has been pointed out that there is a trade-off between an electrolyte's flammability and its performance in a cell. One strategy is to employ gelled polymer electrolytes as alternatives to the currently used organic carbonate electrolytes [39,40]. The polymer electrolytes have high thermal stability, but their lithium-ion conductivity is low, either due to high viscosity or due to low-mobility ion-conducting mechanisms. Another popular means is to add flame-retardants to increase thermal stability and to decrease flammability. The reported flame retardant additives include organic phosphates [34,41–43], phosphites [41,44], triazine [45], organic halogens [46–48], biphenyls [49,50], and a combination of halogens and phosphates [51–53]. The performance of these flame retardants is summarized in Table 1.

The mechanism for organic-phosphate-based flame retardants is well known [54]. When the electrolyte ignites, P$_2$O$_5$ is formed. It then captures the radicals H* and HO* in the flame zone, terminating the chain reactions for combustion. These kinds of additives can significantly improve battery safety by increasing the thermal stability of the electrolytes, but they usually cause the electrochemical performance of the batteries to decrease. In addition, some of them can be reduced onto the anode, either increasing viscosity or forming an undesired SEI layer, thus decreasing ionic conductivity. However, recent developments have been made that address these problems. Several flame-retardant additives reported recently have minimal or no impact on battery performance [34,55]. Moreover, various functional additives, such as EC [49], PC [49], butylene carbonate [49], vinyl ethylene carbonate [56,57], or vinylene carbonate [50,58], have been added as an SEI film precursor to the electrolyte media, which prevent formation of the undesired interfacial layer due to the presence of the flame retardant while improving the electrochemical performance of the cells [48].

3. Processing for electrode fabrication

Typical electrodes for lithium-ion batteries are composites consisting of agglomerated primary particles of active intercalation compounds (called secondary particles), binders, and conductive additives coated and calendared on current collectors. Currently, the most desirable compounds for cathode materials are LiNi$_x$Mn$_y$Co$_{1-x-y}$O$_2$, LiMn$_2$O$_4$ and LiFePO$_4$ based systems. Most of these materials are synthesized in-house through solid-state reactions [59,60], hydrothermal synthesis [61], sol–gel preparation [62], etc. Such active materials are also available from a few companies, including Merck KGaA [63], Nippon Chemical Industrial [64], Samsung SDI [31], Mitsui Engineering and Shipbuilding [65], Seimi Chemical [66], Südchemie [67], Phostec Lithium Inc. [68], but there is little information on the respective synthesis methods in the open literature. Graphite is still the major anode material and is available from Superior Graphite Company [69], Tianeng Graphite Company [70], Hitachi Powdered Metals Co. Ltd. [71], and Sigma–Aldrich, etc. Many types of natural and synthetic graphite are used and their electrochemical performance as anode materials depends on the crystalline make-up, maximum heat-treatment temperature, and furnace processing atmosphere.

3.1. Active particle properties

Properties, such as particle size, shape, morphology, distribution and crystallite size, affect battery performance [72]. A wide range of particle sizes can be found in the literature, from tens of nanometers in primary particles to tens of micrometers in agglomerates. Many efforts have been made to tailor the particle size of cathode

Table 1
Flame retardants and their performance capabilities.

Flame retardant	Electrolyte medium	Performance
Trimethy phosphite (TMP(i)) [41]	1 M LiPF$_6$ in 1/1 EC/DEC (wt%)	TMP (i) reduces the flammability of the electrolyte. It enhances both the thermal stability of the electrolyte and impedance stability of the lithium cells
Trimethyl phosphate (TMP(a)) [41]	1 M LiPF$_6$ in 1/1 EC/DEC (wt%)	TMP (a) reduces the flammability of the electrolyte. It improves the thermal stability of the electrolyte but increases the chare transfer resistance on the cathode side
Tris(2,2,2-trifluoroethyl) phosphate (TFP) [44]	1 M LiPF$_6$ in PC/EC/EMC (3/3/4 and 1/1/3 wt%)	Electrolyte becomes nonflammable with 15 wt% TFP at the expense of 20% loss in ionic conductivity. TFP can increase cycling efficiency of the graphite electrode in PC-based electrolytes by suppressing PC decomposition and graphite exfoliation
TFP [52]	1 M LiPF$_6$ in EC/EMC (1/1 wt%)	TFP (less than 20 vol%) improves capacity retention and capacity utilization
2,4,6-Tris(trifluoromethyl)-1,3,5-triazine (TTFMT) [45]	1.1 M LiPF$_6$ in EC.EMC (4/6 vol%)	5 wt% TTFMT additives shift the peak temperature of oxygen release reaction of the cathode from 270 °C to 330 °C and reduce exothermic heat by 54%. It decreases the electrolyte conductivity from 8.925 to 7.765 mS cm^{-1}. The additive of TTFMT improves both the discharge capability and capacity retention
Cresyl diphenyl phosphate (CDP) [192]	1 M LiPF$_6$ in EC/DMC/EMC (1/1/1 wt%)	The self-extinguishing time (SET) of the electrolyte is 60 s. It is 47 s, 56 s, and 54 s for the electrolyte using CDP, TMP, and TEP, respectively. There are 4.2% and 2.9% losses in the discharge capacity of LiCoO$_2$/Li and graphite/Li with 5% CDP; there are 5.1% and 19.7% losses for TMP, respectively. There are 1.95% and 2.9% losses in the initial discharge capacity and the capacity after 150 cycles
4-Isopropyl phenyl diphenyl phosphate (IPPP) [34]	1 M LiPF$_6$ in EC/DEC (1/1 wt%)	The SEI on the anode surface decomposes at 47, 79, 130, 123 and 181 °C for IPPP concentration of 0%, 5%, 10%, 15%, and 20%, respectively. 5% IPPP additive delays the onset temperature of SEI decomposition by 17 °C, and the heat generation is reduced from −495.5 to −46.7 J g^{-1}. IPPP content below 15% in electrolyte has little effect on cycle efficiency of the battery
Triethyl phosphate (TEP), TMP (a), hexamethoxycy-clotriphosphazene (HMPN) [42]	1 M LiPF$_6$ in EC/EMC (1/1 wt%)	High content (>10 wt%) is required to effectively suppress the flammability of the electrolyte and results in severe degradation in performance. The capacity retention in full cell after 100 cycles follows: HMPN > TEP > TMP (a)
Methyl difluoroacetate (MFA), ethyl difluoroacetate (EFA) [46]	1 M LiPF$_6$ in EC/DMC (1/1)	LiPF$_6$/MFA shows the best thermal stability toward lithium metal or Li$_{0.5}$CoO$_2$, shifting the exothermic peak with lithium metal or Li$_{0.5}$CoO$_2$ to 300 °C. MFA had a better capacity than other fluoroesters. The cycling efficiency is about 80% after 100 cycle times by the method "Li on stainless steel"
Methyl nonafluorobutyl ether (MFE) [47]	1 M LiPF$_6$ in EC/EMC (3/7 vol%)	About 77% of the discharge capacity is achieved with MFE/EMC (8/2 vol%) compared to that with 1 M LiPF$_6$ in EC/EMC (3/7). The discharge capacity can be improved by adding EC
TFP, Bis (2,2,2-trifluoroethyl) methyl phosphate (BMP) (2,2,2-trifluoroethyl) diethyl phosphate (TDP), TMP, TEP, HMPN [51]	1 M LiPF$_6$ in EC/EMC (1/1 wt%)	The ionic conductivity of electrolytes decreases with increasing additive amount and follows: TEP > TFP ~BMP > HMPN. According to the overall performance, TFP seems to be the best choice among these additives

materials for specific performance targets [21,73–79]. Generally, small particles have properties that are beneficial for high power applications: large surface area, short diffusion length, and fast kinetics. In addition, small particles, especially nanoparticles, can accommodate volume change with less risk of crack initiation, and their micro-scaled agglomerates and composite structures provide minimal diffusion path lengths through the electrodes [3]. However, because the electrode has a large surface area, significant side reactions can take place between the electrode and the electrolyte, resulting in severe oxidation of the electrolyte on the electrode surface. This poses a problem with regard to capacity retention and cycle life. Electrolyte oxidation may generate solid products, which may form a passivating layer on the cathode, resulting in larger polarization of the cell [22] and, consequently, cycle-life degradation.

The effect of particle size on cathode performance is summarized in Table 2. It has been reported that capacity retention is better for an LiMn$_{1.5}$Ni$_{0.5}$O$_4$ cathode with a particle size of 70 nm than it is for a cathode with a particle size of 1 μm [21]. The discharge capacity of LiMn$_{1.5}$Ni$_{0.5}$O$_4$ cathodes at low rates with nano-sized particles is higher than it is for cathodes with micro-sized particles at −10 °C, but it is inferior at 25 °C [80]. It has been reported that both capacity and coulombic efficiency increase as LiMn$_2$O$_4$ particle size is decreased from 54 to 20 μm [76]. An LiCr$_{0.2}$Ni$_{0.4}$Mn$_{1.4}$O$_4$ cathode with a particle size larger than 500 nm shows higher discharge capacity and better cycling stability than a cathode with a particle size smaller than 500 nm [30]. However,

the discharge capacity decreases when the average particle size is increased from 1.1 to 3 μm. The capacity of an LiCr$_{0.2}$Mn$_{1.8}$O$_4$ cathode increases with increasing particle size up to 50 nm but decreases with increasing particle size for particles larger than 50 nm [74].

There seems to be an optimal particle size for a given cathode material to achieve optimal performance. The correlation between particle size in cathode materials and their power density and lithium intercalation kinetics was investigated in a prospective thin-layer battery system. Vacassy et al. [81] have reported that an optimal particle size for LiMn$_2$O$_4$ with respect to charge density lies within a range of 0.5–0.8 μm. The specific charge capacity of powders with a large particle size distribution would be superior to nanoparticles having a narrower size distribution, which is ascribed to a better packing density of the powder mixture and enhanced particle interconnectivity inside the cathode.

Grain size has also been reported to affect battery performance. Matsuda and Taniguchi [82] investigated the effect of the grain size of LiMn$_2$O$_4$ particles on cycle performance while maintaining similar particle size. They found that a combination of smaller specific surface area and larger grain size produced better cycle performance. They also reported that the cycle performance for dense LiMn$_2$O$_4$ particles and hollow particles with thicker shells were similar to or better than that for hollow particles with thinner shells. The structure of dense particles and hollow particles with thicker shells remained after 100 cycles; hollow particles with thinner shells developed cracks in the shell structure [72]. The cracks

Table 2
Particle size effect on cathode performance.

Cathode material	Particle size	Lattice parameter (Å)	BET ($m^2\,g^{-1}$)	Comments
$LiMn_{2-x}Ni_xO_4$ [21]	70 nm[a]	8.1684	7–8	Better capacity retention achieved with fine particle, especially at high C rate
	1 μm[a]	8.1686	0.4	
$LiCr_{0.2}Ni_{0.4}Mn_{1.4}O_4$ [30]	55–3215 nm[a]	8.186–8.197	8 to <1	Highest discharge capacity and best cycling stability was achieved with particle size of 1100 nm
$LiMn_2O_4$ [82]	854–1079 nm[a]	8.2399–8.2481	11–14	The smaller specific surface area and the larger crystallite size, the better cycle performance
$LiCr_{0.2}Mn_{1.8}O_4$ [74]	9–1560 nm[a]			Highest capacity achieved with particle size of 50 nm
$LiMn_2O_4$ [76]	19.9, 32.9,41.9 and 53.8 μm			Both capacity and coulomb efficiency increased with decreasing particle size
$LiMn_2O_4$ [81]	Optimum 0.5–0.8 μm		1.7–2.9	The electrochemical performances of powders with large particle size distribution would be improved as compared with nanoparticle of narrower size distribution
$LiCoO_2$ [95]	8.0 μm[b]			VGCFs became hydrophilic after being treated with H_2O_2, which help it disperse in the suspension and improved the discharge performance
$LiNi_{0.5}Mn_{1.5}O_4$ [80]	Nano size and 4 μm[a]			The electrodes with micro-sized particle have better discharge capacity at 20 °C, whereas the electrodes with nano-sized particle exhibit better discharge capacity at −10 °C

[a] Average particle size.
[b] Median diameter.

likely caused a portion of the capacity fading. Huang and coworkers [72] reported that $LiMn_2O_4$ with uniform spherical particles and spherical crystallites showed better cyclability, while an irregular particle morphology and the presence of faceted crystals led to less optimal electrochemical cycling.

The influence of the particle size distribution in a composite electrode has been modeled for constant current discharge assuming that the intercalation ratio is the same for each particle [83]. The first discharge depth can be estimated using an average grain size corresponding to the maximum of the volume distribution for constant standard deviation Gaussian, Gamma, and Fermi distributions, and Gaussian distribution with various standard deviations. The presence of a small fraction of large particles in a composite electrode with a majority of monodispersed small particles lowers the overall capacity. A noticeable increase in the first discharge depth is observed when the largest particles are eliminated from the upper part of the Gaussian distribution.

The effect of particle size and particle size distribution [83] on performance [84–86] and thermal stability [87,88] of the anode is equally important for graphite. The intercalation of lithium ions in graphite electrodes in organic electrolytes involves two steps: transport of the ions in the liquid phase to the edge plane sites of graphite and solid-state diffusion between the layer planes. The intercalation capacity in graphite is limited by the slow solid-state diffusion of lithium ions [85]. Higher capacity tends to be achieved with graphite that has a smaller particle size. However, the initial irreversible capacity loss (ICL) also increases due to the higher surface area, which originates from the decomposition of the electrolyte to form both an SEI layer and gaseous products on the carbon electrode during the initial charge–discharge cycles. The oxidation rate and oxygen chemisorption at the edge sites are much higher than those of the basal plane [89,90]. Thus, the edge sites are the more active for electrolyte decomposition. According to Jiang et al. [87], the fraction of edge sites increases as the particle size decreases, in contrast with the fraction of basal plane sites, for a prismatic graphite. Over the range of particle sizes investigated (2–40 μm), the fraction of basal plane sites dominates (i.e., >94%); however, the small fraction of edge sites plays a major role in the oxidation of graphite. Therefore, compromises in regard to particle size, surface area, and morphology/structure of graphite are needed to obtain the optimum performance at high charge–discharge rates. Particle sizes of 12 and 20 μm are considered to provide the optimum combination of reversible capacity and ICL in the electrolyte for flake [85] and artificial [86] graphite, respectively. The reduced diffusion path and higher surface area of smaller graphite particles facilitate thermally induced delithiation and generate more heat [88]. Consequently, the thermal stability of graphite electrodes decreases with decreasing particle size.

3.2. Active electrode materials processing

According to the type of solvent used, the processing of electrodes can be classified into two categories: water-based (aqueous) and organic solvent-based (nonaqueous) systems [91]. Because 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. This results in stringent requirements of below 10–20 ppm of water, which led industry to focus on nonaqueous systems processed in controlled dry-room atmospheres.

In a typical nonaqueous system, flammable organic solvents are used to obtain a stable suspension with polyvinylidene fluoride (PVDF) as the binder and N-methyl-2-pyrrolidone (NMP) as the solvent. Carbon blacked is added to the electrode components to improve the electronic conductivity of electrodes. There are various formulations of electrode dispersions in the literature and Table 3 summaries some typical cathode formulations. Variation in the formulations is possibly caused by the properties of the components, including particle size, surface area, and conductivity. These properties affect the stability and rheological properties of dispersions. Another important factor regarding the rheological properties of dispersions is solids loading. However, there are few published results in this area [92]. Solids loading depends on multiple factors, including mixing methods and mixing sequences, since these factors affect agglomeration of solid components and viscosity of dispersions [93]. The composite electrodes are fabricated by coating a solvent-based dispersion onto a current collector. This organic system introduces concerns regarding cost, environmental impact, and safety [69,94]. Recently, an aqueous system was adopted to fabricate electrodes [31,67,92,95,96]. Aqueous systems pose less of an environmental hazard and are lower in cost, but they challenge manufacturers to remove any water in the system prior to operation of the batteries.

In such a process, the toxic NMP solvent is replaced by water. Less-expensive carboxymethyl cellulose (CMC) binder (1–2 EUR kg^{-1}) substitutes for PVDF (15–18 EUR kg^{-1}) binder commonly used with the NMP solvent [67]. The systems suffer from powder agglomeration caused by strong hydrogen bonding and electrostatic force introduced by the use of water as a solvent [97].

Table 3
Formulations of various cathode dispersions.

Groups	Electrode composition
Guo et al. [32]	Cr-doped $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ + acetylene black + PTFE (85/10/5 wt%)
Aklalouch et al. [30]	20 mg $LiCr_{0.2}Ni_{0.4}Mn_{1.4}O_4$ + MMM super p carbon black + PVDF-HFP (72/17/11 wt%)
Kunduraci and Amatucci [21]	$LiMn_{2-x}Ni_xO_4$ + super p carbon black + PVDF-HFP + DBP (36.5/9.1/24.5/29.9 wt%)
Matsuda et al. [82]	$LiMn_2O_4$ + Acetylene black (AB) + PTFE (75/20/5 wt%)
Pascual et al. [74]	$LiCr_{0.2}Mn_{1.8}O_4$ + MMM super p carbon black + PVDF (71/17/11 wt%)
Vacassy et al. [81]	$LiMn_2O_4$ + PVA (MW 100000) + graphite (87/3/10 wt%)
Lee et al. [95]	$LiCoO_2$ + graphite (KS-6) and VGCFs + SBR and SMCM (MW 250 000, DS of 1.2) (92.5/6/1.5 wt%)
Kam et al. [193]	$Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ + super P black + PVDF (86/8/6 wt%)
Yao et al. [41]	$LiNi_{0.8}Co_{0.2}O_2$ + acetylene black + PVDF (84/8/8 wt%)
Arai [48]	$LiCoO_2$ + graphite + PVDF (85/8/7 wt%)
Doeff et al. [141]	$LiFePO_4$ + Kynar PVDF + SFG-6 synthetic flake graphite + acetylene black (80/8/6/6 wt%)
Yao et al. [65]	$LiFePO_4$ + ketchen black + PVDF (85/5/10 wt%)
	$LiFePO_4$ + Ketchen black + CMC + PTFE (90/5/4/1 wt%); Cu–Sn + Ketchen black + CMC (93/6/1 wt%)
Wang et al. [158]	MgO-coated $LiCoO_2$ + carbon black + a polymer binder (87/9/4 wt%)
Amatucci et al. [157]	$LiCoO_2$ + super S carbon black + PVDF (85/10/5 wt%)
Lee et al. [194]	$Li[Li_{0.1}Al_{0.05}Mn_{1.85}]O_4$ + Super P carbon black + PVDF (85/7.5/7.5 wt%)
Porcher et al. [195]	$LiFePO_4$/super p carbon/PVDF (80/10/10 wt%)
Ligneel et al. [196]	$Li_{1.1}V_3O_8$/CB/PMMA (73/8/19 wt%)
Li et al. [197]	$LiFePO_4$/KS6/Super P/PBA/SCMC/PSSA (40/1.5/4.6/1.7/3.9/0–4 wt%)

PTFE, polytetrafluoroethylene; PVA, polyvinyl alcohol; VGCFs, vapor-grown carbon fibers; SBR, styrene butadiene; SCMC, sodium carboxymethyl cellulose; PMMA, polymethylmethacrylate; PBA, polybutyl acrylate; PSSA, poly(4-styene sulfornic acid).

The primary need of the aqueous system is to obtain a stable and uniformly dispersed suspension. To this end, additional additives, such as binders and dispersants, are required. For example, CMC and polyacrylic acid (PAA) have been tested in an aqueous-based $LiFePO_4$ paste [94]. The primary function of CMC is as a thickening agent to prevent the nano-sized $LiFePO_4$ particles from precipitation and segregation during processing. PAA is a dispersant for $LiFePO_4$ and can increase the adhesion strength between the cathode composite layer and current collector [98].

Swelling of CMC was found to be critical to the stability of anode graphite suspensions. The maximum swelling ratio and the best discharge capacity were obtained at pH = 7 [99]. Emulsion-polymerized styrene–butadiene copolymer latex was chosen as a binder to enhance the strength of the green graphite electrode sheet [98]. Extra pretreatments, including physical and chemical methods, are needed to disperse carbon material as conducting additive in aqueous systems. Physical methods include ultrasonication, ball milling, grinding, and high-speed shear mixing [100,101]. Chemical methods include using chemical functionalization [102] or surfactants [103], refluxing carbon materials in concentrated acids [104], and using H_2O_2 to oxidize carbon materials [95]. Chemical functionalization or the addition of surfactants can reduce the surface energy of the carbon particles to improve their wetting or adhesion characteristics and decrease agglomeration. Treatment with acids can sever entangled nanotubes and enhance their dispersion as individuals [104]. Oxidation by H_2O_2 can introduce hydrophilic groups such as hydroxyls or carboxyls on carbon materials to enhance their dispersibility [105].

In aqueous systems, the high surface tension of the dispersions may be an issue since this causes poor wettability on current collectors and delamination. This issue can be solved by either decreasing the surface tension of dispersions or increasing the surface energy of current collectors. The surface tension of dispersions can be increased by using a co-solvent or multi-solvent system, such as ethanol–water. The surface energy of current collectors can be enhanced by some heat treatment, such as corona discharge treatment (CDT) or plasma treatment. It has been demonstrated at Oak Ridge National Laboratory (ORNL) that the surface energy of an aluminum current collector was increased from 30 to >60 mN m^{-1} after CDT.

3.2.1. Electrode deposition and fabrication

Many techniques have been applied to fabricate electrodes for lithium-ion batteries, including chemical vapor deposition [106–109], electrostatic spray deposition [110–115], pulsed laser deposition [116–120], radio frequency sputtering [121–123], spin coating [124–126], screen printing [127,128], ink-jet printing [129,130], and the molten carbonate method [131]. A thorough overview of these techniques is provided by Li et al. [132]. In addition, techniques based on tape casting and slot-die coating are under development in our research group at ORNL to fabricate large-scale electrodes. The effect of variable parameters, including the suspension formula and drying conditions, on the electrochemical performance of electrodes is being investigated and will be addressed in future publications.

Recently, three-dimensional (3D) batteries have been proposed to miniaturize battery size [133–135]. In contrast to the in-plane surface in traditional electrodes, the out-of-plane dimension in a 3D configuration may enable the battery to have a small areal footprint. The 3D configuration may also provide a shorter diffusion path length for lithium ions between anode and cathode and a higher electrode surface area [133]. Some 3D architectures are achieved by depositing thin films in a 3D arrangement using a micro-channel plate as a substrate [136]. In other 3D configurations, there are vertical "posts" connecting to a substrate with the layered battery structure formed around the posts [137]. Still other 3D architectures are based on the conformal deposition of electrode and electrolyte layers on a graphite mesh as anode and cathode current collectors [138]. However, current approaches to 3D batteries are expensive and have a low potential for scalability, which limit 3D batteries to small-format, niche applications.

3.2.2. Electrode modification and optimization

The rate capability of batteries is determined by the kinetics of the charge–discharge reactions and the mobility of lithium ions to and from their final intercalation sites. The rate performance of the cathode material appears to be the bottleneck in the development of lithium ion batteries with high rate capability [139]. Different methods have been attempted to improve the rate performance of the cathode materials, including adding a conductive coating such as carbon [140–143] or metal powder [144–146].

Lithium-ion batteries may overheat or even undergo a thermal runaway [147] during high current drain. The thermal stability of the anode is of critical importance for mitigating the possibility of thermal runaway. Exothermic reactions associated with carbonaceous anode materials are initiated with SEI layer decomposition and are followed by reaction of the intercalated lithium with the electrolyte, electrolyte decomposition, and a carbothermal reac-

tion of carbon anode materials [148]. Extensive efforts have been attempted to improve the thermal stability of lithium-ion batteries, such as adding a flame retardant to electrolytes [34,41–43] or encapsulating the particles of active materials [143]. One strategy is coating the graphite surface, which can effectively suppress the irreversible intercalation of the solvated species and the side reactions leading to the formation of an SEI layer [149–155]. For example, graphite coated with thermal-vapor-deposited carbon showed a significant decrease in initial irreversible capacity loss and an increase in coulombic efficiency [143]. The carbon coating on graphite particles suppresses the decomposition of PC on the anode and subsequent exfoliation of graphite. Mild deintercalation of the carbon-coated natural graphite at elevated temperatures leads to a lower heat evolution than that of the unmodified graphite [148]. Such coatings increase the thermal stability of the graphite anode and improve the discharge capacity and capacity retention [156].

Another issue for cathodes is the dissolution of tetravalent ions from the active materials into the electrolytes [157]. For example, the dissolution of tetravalent ions, such as Mn^{4+} and Co^{4+}, could degrade the cathode by causing a loss of active material and by forming an inactive phase, such as Co_3O_4, in it [158,159]. Extensive efforts have been made to modify cathode surfaces to enhance their cyclability. Most surface modification involves coating the cathode particles with an oxide, such as Al_2O_3 [160], B_2O_3 [160], SnO_2 [161], MgO [63,158], or TiO_2 [162]. The surface coating may improve the cycling stability of cathode materials by physically separating the oxidized active material from the electrolyte [163,164]. However, the coating mechanism is not yet fully understood [64].

Two main approaches to modifying electrodes have been adopted: coating active material particles [160] and coating finished electrodes [152,165]. Coatings on active materials are accomplished by sol–gel, precipitation and thermomechanical methods. In the sol–gel and precipitation techniques, metal in the form of nitrates is added to a solution with active materials. Then the fine metal particles are deposited in situ onto the particles of active materials when the nitrates are chemically reduced [144,145].

Carbon is formed by high-temperature carbonization of pyromellitic acid or polyvinylchloride dissolved in a solution with active materials [141] or mechanically mixed with graphite particles [149,154]. Carbon can also be coated onto the graphite particles by thermal vapor decomposition of toluene at 1000 °C [143].

Oxides are formed and deposited by hydrolyzing metal compounds, such as alkoxides, followed by an annealing process [160,166]. In the thermomechanical process, oxides are dispersed in a solvent first and then mixed with the active material by sonicating and stirring. After a subsequent slow evaporation of the solvent, the oxides remain as a coating on the particles of active material [162]. The thermomechanical process is cost-effective. The cyclability of TiO_2-coated $LiCoO_2$ is better when the thermomechanical process is used than when the sol–gel process is used [162].

Recently, Gao et al. coated a layer of silver onto a graphite electrode [152] and found that the Ag-coated graphite electrode can significantly suppress PC decomposition and graphite exfoliation. Charge-transfer resistance decreased, and the diffusion coefficient of Li ions increased. However, silver is not expected to be introduced into large-scale energy storage devices.

4. Separator

A separator is placed between the cathode and the anode to prevent contact. A good separator should have high ionic flow, negligible electronic conductivity, good wettability, high chemical stability against electrolytes, high mechanical and dimensional stability, and sufficient physical strength to withstand the assem-

bly process. If a lithium-ion battery is short-circuited, the separator should also be designed to stop ionic flow and prevent thermal runaway. This is often accomplished by melting all or parts of the separator, filling the pores and fully preventing ions from flowing from one electrode to the other. Thus, the battery reactions are suppressed. A good overview of separators is provided by Arora and Zhang [167]. Separators in most batteries are made of either nonwoven fabrics or microporous polymeric films [167]. The nonwoven fabrics consist of a single polyolefin or a combination of polyolefins. They usually are made by adhering or hot-welding fabrics together [168]. However, it is difficult to fabricate a thin (25 μm) nonwoven fabric with desired physical properties. Thus, microporous polymeric films made of polyethylene and polypropylene are preferred as the separators in commercial lithium-ion batteries. Recently, composite films consisting of components with different melting temperatures have been developed [169–171]. The low-melting-point component acts as a thermal fuse while the high-melting-point component provides physical integrity [168].

Separators in lithium-ion batteries are manufactured through wet processes [172] and dry processes [173]. Each employs one or more orientation step to impart porosity and/or increase tensile strength. The dry process involves melting a polyolefin resin, extruding it into a film, annealing, and forming micropore initiators and micropores through orientation at low temperature and high temperature, respectively [168,174]. A detailed description of this process is provided by Sarada and coworkers [175]. The wet process involves mixing a low-molecular-weight substance, such as a hydrocarbon liquid, with a polyolefin resin; heating and melting the mixture; extruding the melt into a sheet; orienting the sheet either biaxially or in the machine direction; and then extracting the liquid with a volatile solvent [167,168,176].

Separators obtained by the dry process are available from Celgard [177,178] and Ube [179]. Separators obtained by the wet process are available from Tonen [174], Asahi Kasei [180], Mitsui Chemicals [181], and Entek. The polymeric films are inherently hydrophobic, which results in poor wettability and poor electrolyte uptake [182,183]. Therefore, various methods have been adopted to improve their hydrophilicity, such as radiation-induced graft polymerization, plasma treatment, surface polymer coating, chemical treatment, and impregnation of a gel polymer electrolyte [184–188]. Among these methods, the radiation-induced graft polymerization is superior and does not require any initiators. High-energy electron beams can create large quantities of radicals, form active sites uniformly for initiating grafting through the matrix quickly, and react mildly [189]. This technique has been adopted commercially to produce ion-exchange membranes that are used as battery separators [190].

A new direction in lithium ion battery separator research is the addition of ceramics and metal oxides to the separator polymer solution to form highly filled polymer composites. This modification to the conventional polymer separator is thought to improve the short resistance, as well as the thermal and mechanical properties during battery operation. To date, there is little information available on the processing methods related to these novel composite separators.

5. Cost assessments

Currently, the cost of lithium-ion batteries is still too high. For example, the cost of 18,650 cells is approximately $1700 [2,3], twice of the target price on a kW basis for HEVs. The cost of lithium-ion batteries is approximately 3–5 times of the target price on a kWh basis for PHEVs [191]. The main components of battery costs are materials, labor and overhead. The cost of materials is the most significant part. It makes up over 80% and 90% of the total costs of high

power and high energy batteries, respectively [2]. Therefore, the potential for reducing costs of lithium-ion batteries lies in achieving low cost materials and materials processing. It is especially important to lower the cost of cathode materials since they make up over 70% of the total cost for high power batteries [2]. To this end, novel methods that can synthesize large amounts of cathode materials with low cost raw materials need to be developed. Development of novel cathode materials with higher capacity and/or a wider state of charge is an alternative solution which reduces the required amount of cathode materials and, thus, the battery size. In addition, improvement in processing of cathode slurries can also significantly reduce the cost. The cost of $LiNi_xMn_yCo_{1-x-y}O_2$ is $90 \, kg^{-1}$ (Toda America) and it is $108 \, dm^{-3}$ (Sigma–Aldrich) for NMP. The viscosity of cathode dispersions can be dramatically decreased with desired mixing methods and appropriate mixing sequences. This can reduce the amount of NMP and, which in turn reduces the processing cost. The mixing methods and mixing sequences are even more important for anode processing since it usually requires a larger amount of NMP.

Other areas with potential to reduce overall battery cost include chemistries and/or electrode designs for lower electrode area and smaller battery size, higher coating speed for faster manufacturing process, etc. [191].

6. Summary

There is little doubt that materials processing and material development are critical to improving lithium-ion battery performance. Much effort has been made in fabricating each component of lithium-ion batteries. However, it is far from enough. More work is required to optimize the processing conditions and to understand the effect of the processing on battery performance. For example, there is controversy in understanding the role of surface coating in improving the cyclability of lithium-ion batteries. Further work is needed to improve the cyclability, lower the costs, and reduce the environmental hazards associated with the manufacture of large-scale batteries for hybrid and electric vehicles. To that end, a shift from a nonaqueous system to an aqueous system for fabricating composite electrodes might significantly reduce the battery cost and environmental effects. Comparable results can be obtained from an aqueous system such as those in conventional batteries. However, how to stabilize aqueous solutions and reduce the amount of remaining water are key points and have yet to be fully demonstrated.

Acknowledgments

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