Journal of Power Sources 196 (2011) 2452–2460

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Review

Materials processing for lithium-ion batteries

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ARTICLE INFO

Article history:
Received 29 September 2010
Received in revised form 28 October 2010
Accepted 1 November 2010
Available online 9 November 2010

Keywords:
Lithium-ion battery
Materials processing
Cathode
Anode
Separator

ABSTRACT

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.

Contents

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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doi:10.1016/j.jpowsour.2010.11.001

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_2O_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 $LiNi_xMn_yCo_{1-x-y}O_2$, $LiMn_2O_4$ 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