EFFECT OF COATING ON DIFFERENT COMPONENTS OF THE LITHIUM BATTERIES FOR ENERGY STORAGE

Abstract

 Energy storage has grown into a key area of research for both industry and academia in recent times, as the energy issue has gotten worse. Surface coatings play a significant role in the energy storage of various types including chemical, electrochemical, electrical, mechanical and thermal energy. Surface coatings are barriers that are artificial often comprised of electrochemically active or inactive coating materials, placed to the surfaces of different components of lithium ion batteries (LIBs) to provide a better electrochemical performance of the materials by limiting the potentially damaging side reactions. The selection of the right coating material and thickness is crucial which helps in improving different characteristics of the different components of batteries. By expanding the surface area, coatings also assist in improving the efficiency of storage systems. It is possible to incorporate coating materials directly into substrates without the need for further morphological deformations. This chapter focuses on the effect of coating on the different components of LIBs and its usage for energy storage.

Keywords: Energy storage materials, coating, lithium ion batteries coatings, energy storage systems

Authors

Devyanshu Sachdev

Department of Chemical Engineering & Technology Dr. Shanti Swarup Bhatnagar University Institute of Chemical Engineering & Technology, Panjab University Chandigarh, India.

Navneet Kaur Bhullar

Department of Chemical Engineering University Institute of Engineering Chandigarh University Mohali, Punjab, India.

Kamlesh Kumari

Department of Chemical Engineering Sant Longowal Institute of Engineering & Technology (SLIET) Longowal, Punjab, India.

I. INTRODUCTION

The outstanding overall performance of LIBs in all aspects, including cost and electrochemistry, has attracted a lot of attention lately [1]. They are extensively used as power sources in numerous kinds of applications because of their high energy densities, high coulombic efficiency, low self-discharge characteristics and wide range of chemical potentials accessible with different electrode designs [2]. The evolution of LIBs next generation with high charge capacities and power densities for electric vehicles (EV) and hybrid electric vehicles (HEVs) which finds applications in aerospace and automotive electronic devices, in particular, has become growing in significance over the past ten years [3–6].

The most significant barrier in battery design is to ensure that electrodes stay in good shape which will result in batteries with outstanding capacity retention and a long cycle life. The different characteristics of different components of the batteries such as cathode, anode, electrolyte and separator are improved via modification by coating some polymer nanocomposites, inorganic particles and inorganic/organic composites [7–9]. The enhancement of thermal and electrochemical stability of the materials of the batteries plays an important role by introducing different types of coatings such as polymer, metal oxide and metal-based coating which further helps to mitigate unfavorable side reactions which enhances the performance of the batteries [10–13]. In context of surface engineering, a coating is a layer of material that is applied to a substrate in order to enhance the surface characteristics and provide various sorts of protection including resistance to corrosion, abrasion and other factors. The size and shape of the component, the service environment in which it will be used, the anticipated duration of its useful life, the underlying materials that are suitable with it, the cost and other variables all play a role in choice of a coating for the for each component of the LIBs. The different applications for the coatings include antibacterial, anti-corrosion, anti-fouling, energy storage, fire resistance, optical, self-healing, scratch resistance and shock resistance [14,15].

II. DIFFERENT COMPONENTS OF LITHIUM-ION BATTERIES

1. Cathode Materials: The significant proportion of cathode materials are transition metal oxides that can be oxidized to higher valences when lithium is eliminated [16,17]. Although oxidizing the transition metal can keep the compound's charge neutral, substantial composition changes cause numerous phase transitions, necessitating the use of crystalline composition which are stable throughout across a wide range of composition. The charging process, when the majority (preferably all) of the lithium is withdrawn from the cathode, presents a unique challenge for this structural stability. During the discharge, the introduction of lithium into the cathode material, and electrons from the anode lower the valence of the transition metal ions there. The maximum discharge current is governed by the rates of these two processes as well as the accessibility of the lithium ions in the electrolyte to the electrode surface. The cathode's performance is heavily influenced by the electrode's microstructure, morphology and inherent electrochemical properties because exchange of lithium ions with the electrolyte takes place at the electrode-electrolyte interface. There has been a lot of research done on the usage of nano-structured electrodes with high interfacial and surface areas to enhance the performance $[18-22]$. LiCoO₂ is the cathode material that is most frequently implemented in LIBs [23] which develops the a -NaFeO₂ structure, a distorted rock-salt structure where the cations are arranged in the alternate (111) planes. This arrangement creates planes of lithium ions across which lithiation and delithiation can take place [24]. The alternative cathode materials are being explored in order to reduce cost and increase stability, not withstanding $LiCoO₂$'s effectiveness as a cathode material. The different class of materials such as lithium-nickel based materials, lithium manganese-based materials, vanadium-based materials and phosphate-based materials are better in some or another form in comparison to $LiCoO₂$. The α -NaFeO₂ structure of $LiNiO₂$ provides the lower cost and higher energy density but it less ordered and less stable in comparison to LiCoO₂ [25,26]. In another set of promising materials, LiMn₂O₄ in which manganese occupies the octahedral sites whereas the tetrahedral sites are predominantly occupied by lithium which further forms the a spinel structure $(Fd\overline{33}m)$ which reduced the cost and is safer in comparison to $LiCoO₂$ but it has inferior capacity in comparison to the a -NaFe $O₂$ structure [27–29]. In addition to that there is a phase change occurs during cycling for $LiMnO₂$ [30,31]. In another set, the vanadium oxide forms layered compounds which has multiple valences which makes it a potential material as a electrode material forms orthorhombic and monoclinic for V_2O_5 and Liv_3O_8 respectively which provides a high capacities but relative low voltages [16]. The phosphates can also be a promising category of cathode materials having olivine structure (Pnma) i.e., $(LiMPO₄)$, in which tetrahedral sites are occupied by the phosphorous whereas octahedral sites are occupied by transition metal. In addition to that, one-dimensional chains of lithium are formed along the (010) direction [32].

2. Anode Materials: Anode is one of the essential components for the LIBs. Presently, anode material has more potential for advancement than the cathode material. The negative electrode of LIBs was the initial application of lithium metal but due to the ease with which dendrites might develop during the reaction, its commercial use was constrained. There has a been a variety of materials which are being used as anode materials which can be assorted into carbon-based materials, alloying-based materials, transition metal oxide-based materials and metal organic framework-based materials which is due to their enormous porosity and surface area [33]. Over the past 20 years, negative electrode materials made of graphite have been increasingly popular since they are secure and safe for the environment. Nevertheless, there are disadvantages to graphite-based negative electrode materials as well. Specifically, their low specific capacities resulted in problems with low computational efficiency and poor rate performance, which are currently the main reasons why LIBs operate poorly. Therefore, a lot of time and effort has been put into finding appropriate materials for anode but often improving one aspect of performance means sacrificing other qualities. The application of novel materials from MOFs in LIBs is depicted in **Table 1**.

Table 1: Application of Novel Materials from MOFs in LIBs. Reprinted with Permission from Elsevier [33]

3. Electrolyte Materials: The solid electrolyte's incorporation simplifies cell design, elevates safety and durability and does away with the necessity to contain the liquid electrolyte. Inorganic ceramics and organic polymers are the two main categories of materials utilized as solid electrolytes in LIBs [46] . The mechanical qualities are the most noticeable distinction between these types. Ceramics are better suited for stiff battery designs than other materials such as thin film based devices, because of their large

elastic moduli. Contrarily, flexible battery designs benefit from the low elastic moduli of polymers. Additionally, polymers are typically simpler to producer than ceramics, which lowers the cost of production. Ceramics, on the other hand, are better suited to hotter or more hostile settings. The ionic conductivity data from the literature and compares them using Arrhenius-type graphs [46] . This compilation serves as a basis for comparing different electrolyte systems and determining the conductivity ranges for various electrolyte materials. The different classification of electrolyte is depicted in Fig 1 [46,47].

Figure 1: Different Classifications of Electrolytes for LIBs

4. Separator Materials: The separator has the characteristic of a porous substance which enables lithium ions to pass through it while also serving as electrical insultation between the electrodes. A lithium-ion cell's safety and performance depend on the electrolyte's wettability and the contact between the electrodes and separator. To prevent an internal short circuit, the separator also needs to be able to maintain insultation between the electrodes [48]. In the assembly operations for jelly roll and z-fold stack cells, the separator must be mechanically robust enough to endure the stress and compression experience during winding [49,50]. In separator rupture caused by mechanical stresses should be decreased by increase in the mechanical strength [51] whilst higher separator thermal stability can delay the process of melting [52,53]. An internal short circuit event could result from melting or rupturing of the separator [54–56]. **Figure 2** illustrates the flowchart which depicts the importance of separator in the LIBs.

Figure 2: An illustration of the thermal runaway process in a flow chart that emphasizes the crucial roles of the separator and the liquid electrolyte. Reprinted with permission from Elsevier [57].

III. COATING ON DIFFERENT COMPONENTS OF LITHIUM ION BATTERIES

1. Cathode: The ability of surface coating for improving different characteristics of LIBs such as thermal stability, capacity retention and rate capability. The different classes of coating materials have been investigated which includes carbon, metal oxides, metal carbonates, metal aluminates, metal fluorides, metal phosphates [58]. The researchers from China worked on the $Li_{1,2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ coated with CaF₂ as cathode materials for LIBs which helped in enhancing the electrochemical efficiency of 91.2% of 0.2 C after 80 cycles for coated specimen and showed a discharge capacity of 190 mAh g^- ¹ at 1C after 100 cycles which was higher in comparison to the pristine specimen which might be attributed to the stable structure of the electrolyte/electrode interface, the rapid

transition from the layered phase to the spinel phase, and the suppression of electrolyte decomposition [59]. The investigation on Ni-rich layered oxide $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.2}\text{O}_2$ cathode material coated with dihexadecyl phosphate showed an initial capacity of 168.7 mAh g^{-1} at 2 C in comparison to 134.7 mAh g^{-1} for pristine specimen [60]. Another research group from China worked on the $FePO₄$ coated on $LiCoO₂$ and after 400 cycles, LiCoO₂ still performs electrochemically well with initial discharge capacities of 146 and 155 mAh g^{-1} and higher capacity retention of 88.7 and 82.5% respectively [61]. The researchers from Australia and China investigated on the design and fabrication of cathode $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ which was doped with Al and coated with LiAlO_2 which employs an oxalate-assisted deposition and subsequent thermally driven diffusion approach which has enabled the Ni rich cathode to maintain 97.4% cycle performance after 100 cycles and 127.7 mAh g^{-1} with a rapid charging capacity and capacity loss of 5.6% only at 20 C for a 500 long cycle life [62]. The investigation on double coated nickel-based cation disordered cathode for LIBs with carbon-Al₂O₃ coating in which C/AI_2O_3 coated oxide provided improved long term electrochemical performance with better capacity and cycling retention (around 149 mA h g^{-1} after 200 cycles at 40 mA g^{-1} equal to the capacity retention of 76.1%) that reported Ni based DRS oxides [63]. In addition to demonstrating a high specific capacity of 135 mAh g^{-1} at 10 C, the development of Ti doped and LiYO₂ coated on a Ni rich cathode for LIBs also revealed no capacity loss at 1 C for 100 cycles [64]. **Figure 3** illustrate the typical families of cathode materials [65].

Figure 3: Typical families of cathode materials

2. Anode: The coating on the anode of LIBs has a significant impact on the overall performance, durability and safety. The coating provides essential characteristics such as enhancement of safety, protection from undesirable reactions and significantly improved stability and cycle life. The researchers from Huazhong University of Science and Technology, China have investigated development of a facile and efficient by combining ball milling and chemical vapor deposition (CVD) method for obtaining carbon coated nanosized $Li₃VO₄$ for enhancement conductivity of the material whereas compared to its untreated counterpart, this modified $Li₃VO₄$ has better rate performance, a higher reversible capacity (from 225 to 315 mA h g^{-1}), and a higher first-coulombic efficiency (from 68.8% to 79.5%) [66]. In addition to that, the carbon coated nanosized Li_3VO_4 with

only 5% conductive additive exhibits better performance than the micro sized raw $Li₃VO₄$ with 10% conductive additive, showing the important effect of particle size and electronic conductivity on the electrochemical characteristics of $Li₃VO₄$ [66]. The researchers from China and Canada collaborated to develop the anode in which the $SiO₂$ nanotubes were coated with biomass derived carbon materials due to which it helped to enhance the conductivity and in addition to that the uniform dispersion of SNTs-@C-PLDF in particular exhibited the finest electrochemical performance corresponding to which it also exhibited high specific capacity and excellent rate capability of 661 mAh g^{-1} and 262 mAh g^{-1} respectively at 3000 mA g^{-1} [67]. SNTs-@C-PLDF exhibited a capacity of 549 mAh g^{-1} at 1000 mA g^{-1} after 800 cycles with improved cycling stability. The logic behind the remarkable performance of SNTs@C-PLDF can be attributed to hollow structure of SNTs coupled with highly developed 3D electrode and in addition to that the Li⁺ movement and account for the SNT's changing volume cycle which help in having high capacity and high cycling life and rate [67]. The Si anode in LIBs were coated with aluminum oxynitride through atomic layer deposition [68] which helped to elevate the capacity retention to 72.3% in comparison to 13.3% for the bare Si electrode. The promising cycle stability was also observed i.e., after 140 cycles, the reversible capacity increased from 331 mA h g^{-1} for bare Si electrode to 1297 mAh g^{-1} for AlO_xN_y-coated one, and the capacity retention increased from 13 to 72% with the ideal AIO_xN_y coating (~2 nm) [68]. After cycling, it was observed that the coating considerably reduced the charge transfer and solid electrolyte interface resistance and preserved the structural integration of Si electrodes by preventing electrode delamination and electrolyte degradation from the current collector [68]. **Table 2** represents the comparison of coated with anode for LIBs.

Anode material	Type of coating	Current density $(A g^{-1})$	Capacity $(mAh g-1)$	No. of cycles	Ref.
Graphite	AlF ₃			300	[69]
Silicon	Carbon		HAR: 800		[70]
Silicon/	Polydopamine	0.1	RC: 1946	100	$[71]$
graphene/ CNT	carbon				
Sn/SnO ₂	NDC	0.1	DSC: 1058	100	$[72]$
			RDSC: 486.5		
MoO ₃	Carbon		1064	50	$[73]$
3D NDC/SnO ₂	Polypyrrole	$\mathbf{1}$	RC: 591	1000	[74]
SiO_x/C	Carbon coating	0.1	RC: 702	200	$[75]$
nanotubes					
FeS ₂ @C	RGO		HSC: 820.7	300	[76]

Table 2: Comparison of Coated Anode Materials for LIBs

HRC: High reversible capacity; RC: reversible capacity; NDC: nitrogen doped carbon; DSC: Discharge specific capacity: SC: specific capacity; RDSC: reversible discharge specific capacity; RGO: reduced graphene oxide

3. Electrolyte: The high-performance rechargeable LIBs are the most significant energy

storage technology among several technologies available for energy storage technologies [77,78] because of their high energy density and lengthy life-span. The commercial LIBs with liquid electrolytes and ester carbonates, on the other hand, are highly flammable and readily cause safety mishaps while in use [79,80], which restricts their use in a wider range. All solid-state electrolytes have an advantage over conventional liquid electrolytes due to its non-flammability and non-leakage, it emerged as a high-priority solution to the problem. The coating plays an significant role in the enhancement of different characteristics for the electrolyte of LIBs. The researchers from Tsinghua University investigated on the Li-La-Zr-O thin films prepared by sol gel technique which were further annealed for a temperature range of 600-800˚C which showed a reduction in the ionic conductivity from $1.67*10^{-6}$ S cm⁻¹ for 600°C to $8.53*10^{-7}$ S cm⁻¹ for 800°C which was due to decreased in lithium concentration, increased defect concentration and enhanced impurity phase [81]. Another group from Austria developed from propylene sulfite-based film forming electrolyte additive for LIBs in which they developed a electrolyte LiClO4/propylene sulfite/propylene carbonate (95:5 by volume) showed a high oxidation stability at a $LiMn₂O₄$ cathode due to which it showed a great interface behavior [82]. The $Li₂CO₃$ layer on the graphite substrate helped in increasing reversibility in the development of solid electrolyte interface which helped in enhancing the stability at the elevated temperatures and in addition to that it exhibited superior stability at elevated temperature, inferior self-delithiation in storage and higher capacity retention over prolonged cycling [83]. The scientific community from Germany developed an electrode/electrolyte which showed an excellent cycle performance for LIBs by slurrybased technology due to its easy production and homogenous nature of the cathode and electrolyte. The combination of double coating and cold pressing ensured a great interaction between composite cathode and solid electrolyte layer and in addition to that the proportion of all components (active material, sulfidic solid electrolyte, carbon and binder) which assisted in delivering the superior performance [84]. It was observed that the materials with the lower porosity and lower surface area showed a better electrochemical performance whereas the solid polymer electrolytes are utilized to protect the Li anode and achieved the initial capacities of $140 \text{ mA} \text{h} \text{g}^{-1}$ whereas the comparison of NCM622 in liquid electrolyte cells showed improvement in the capacities (165 mAh g^{-1}) [84]. The Chinese researchers worked on surface modification of $LiCoO₂$ with solid electrolyte film of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)$ ₃ (LATP) which was developed using a facile solution method that helped in enhancing the electrochemical and structural characteristics at a higher voltage in the half cell with liquid electrolyte. In addition to that the LIBs with PEO based polymer electrolyte modified with 0.5 wt% of LATP which showed superior capacity retention (93.2% after 50 cycles) at high potential of 4.2 V and LATP helped in suppressing the oxidation of PEO at higher voltage [85].

4. Separator: In order to increase the performance and safety of LIBs, the coating on the separator is a crucial component. The performance parameters which are enhanced by coating separator such as improved electrochemical performance, improved thermal stability, enhanced safety, reduced internal resistance and electrolyte control. The researchers from China worked on the coating poly(vinylidene fluoride-cohexafluoropropylene) with polyimide which exhibited high ionic conductivity of 1.79 mS cm⁻¹ and excellent mechanical characteristics that also enhances the electrochemical performance i.e., even after 300 cycles at 0.1 C it has retained 77.4% of original capacity and it also has a high heat tolerance, high cycle stability and can function correctly after

being heated under 140°C for 1 hour [86]. The another research group from China developed a polyacrlonitrile/poly(vinylidene fluoride-co-hexafluoropropylene) was stimulated with mussel which showed an outstanding electrolyte retention and high porosity of 553.23 % and 82.09% respectively. In addition to that, it also showed an excellent electrochemical performance with excellent ionic conductivity, high specific capacity, wide electrochemical stability window and cycle stability after 600 cycles with r capacity of 2.81mS cm⁻¹, 147 mAh g⁻¹ at 1C, ~5.25 V and 120 mAh g⁻¹ respectively [87]. The scientists from Korea investigated on the influence of size of piezoelectric materials on a separator coating layer which was used for suppressing dendritic Li growth in LIBs which showed that the nanosized particles developed a dense electric field which enables a deposition of Li uniformly due to which it also showed a better electrochemical performance in comparison to its counterparts during 150 cycles [87]. The investigation on the effect of concentration in ceramic/co-polyamide coated polypropylene separators for LIBs in which it was observed that polyimide binder and Al_2O_3 ceramic in which effectively thwarted the thermal transfer shrinkage (at 150˚C), 10% whereas the Poly(vinylidene fluoride/hexafluoropropylene (PVDF-HFP)) coated propylene separators significantly reduced the unit's internal short circuit whereas the PVDF-HFP exhibits half cells linked to separator thermal shrinkage (100 minutes at 160˚C) only 40 minutes under the same circumstances [88]. The scientist from Korea investigated on the binder-less grafting of $SiO₂$ nanoparticles onto polyethylene separators for LIBs which exhibited reduced thermal shrinkage ($\leq 5\%$ at 120°C), superior ionic conductivity (0.84mS cm⁻¹) and stronger adhesive strength (>2.5 N cm⁻¹) than the traditional coating comprising of ceramic particles. In addition to that it also exhibited an excellent rate capability and cycling performance of 68mAh g^{-1} at 5C and 143 mAh g^{-1} after 200 cycles respectively [89]. **Table 3** depicts the comparison between the different coating on the different separator material and their characteristics.

IV. SUMMARY

 In summary, with the intensifying of the energy crisis, energy storage has emerged as a major topic of research interest for business and the academic community. The need for surface coatings that can store energy mechanically, electrically, chemically, electrochemically and thermally is critical. Materials that are electrochemically active or inert are often used to create surface coatings which is well known that these coatings help in reducing charge transfer resistance across interfaces. The choice of proper coating material is essential for improving electrochemical performance. As more innovative battery materials with some form of surface coating are developed, an in-depth investigation of their impact in lowering cathode material cycle life problems is essential. Coatings assist in enhancing storage systems efficiency by expanding their surface area. Without further morphological deformations, coatings ingredients can be injected into the substrates.

V. ACKNOWLEDGEMENT

The authors express their gratitude to Department of Chemical Engineering, Chandigarh University for their cooperation in completing this study.

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