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Electrical modification of a composite electrode for room temperature operable polyethylene oxide-based lithium polymer batteries

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Abstract

Lithium polymer batteries (LPBs) are considered to be the most promising alternatives to current lithium-ion batteries (LIBs), which have been known to exhibit certain safety issues. However, the relatively poor electrochemical performances of LPBs hinder their practical usage, particularly at high C-rates, moderate temperatures, and/or with high loading densities. Therefore, this study analyzes the use of a novel composite electrode for manufacturing room-temperature operable LPBs with high loading densities. Rapid decay in the rate capabilities of LPBs at high C-rates is found to be attributable to the increased electrical resistance in an electrode. To account for this, this study modified the composite electrode with various conducting fillers. Subsequently, the effect of the type and content of the conducting fillers on the performance of LPBs was systematically investigated using the composite electrode. The incorporation of the conducting fillers in the lithium iron phosphate (LFP) composite electrode was found to effectively reduce the electrical resistance and consequently improve the electrochemical performance of LPBs. Furthermore, LFP composite electrodes with a mixture of structurally different graphene (G) and carbon nanotube (CNT) (1 wt%) were observed to demonstrate synergistic effects on improving the electrochemical performance of LPBs. The results obtained in this study elucidate that the facilitated electrical conduction within a composite electrode is critically important for the performance of LPBs and the expedited diffusion of Li⁺.

1. Introduction

Lithium-ion batteries (LIBs) are widely used in portable electronic devices, electric vehicles, and energy storage systems, due to their high energy density and stable cycling performances [1–3]. Considerable attention has been given to the safety issues associated with LIBs, particularly when their energy densities are increased. Currently available LIBs usually employ intrinsically flammable organic liquid electrolytes, which pose a fire or explosive hazard when the battery temperature rises sharply [4–6]. In order to solve the safety issues associated with the use of liquid electrolytes, polymer electrolyte (PE) system, such as ionic liquid PE (ILPE), gel PE (GPE), and solid PE (SPE), has been considered as a fascinating candidate electrolyte system [7–9]. Among the several PE systems, ILPEs and GPEs have higher ionic conductivity in comparison to SPE, and also have several advantages such as broad electrochemical stability window, non-flammability, and desirable flexibility. However, they intrinsically
include liquid component and thus still remain one issue of electrolyte leakage. On the other hand, SPEs do not have the leakage issue and have been regarded as the most promising electrolyte system to overcome the safety issues associated with existing LIBs. LIBs that utilize SPEs are referred to as lithium polymer batteries (LPBs) and exhibit several advantages over existing LIBs, including fire resistance, elimination of leakage, high energy density, and physical flexibility [10–14].

Since the discovery of the ionic conductivity of polyethylene oxide (PEO) complexes by Wright [15], further research has primarily focused on PEO-based SPEs. That is because PEO has been considered as one of the most promising candidates for polymer electrolyte [16]. Ether groups in the PEO backbone can provide pathways for cation migration, thus supporting support fast ionic transport. PEO can also easily form complex with many alkalis salt, thus having high solvation power [9]. However, the ionic conductivities of PEO-based SPEs are relatively poor at room temperature. Accordingly, significant efforts have been devoted to improving the ionic conductivity of PEO-based SPEs by suppressing the crystallinity of SPEs through polymer blending [17], copolymerization [18, 19], cross-linking [20], or hybridization with inorganic particles for room-temperature operable LPBs [21, 22]. Efforts have also been made to address the high contact resistance between SPEs and electrodes and the expedited Li-ion diffusion in relatively thick electrodes. The most promising way to enhance Li-ion diffusion within an entire cell is to introduce a composite electrode that contains Li-ion conducting materials [23–27]. Several studies have clearly demonstrated that the interfacial contact can be significantly improved by using the in situ polymerization method, which involves the infiltration of a SPE precursor solution into the composite electrode prior to its polymerization [28–30].

The above-mentioned efforts can play a significant role in the improvement of the performance of LPBs. However, enhanced rate capabilities at relatively high C-rates and moderate temperature are still difficult to achieve with relatively thick electrodes [23, 24, 28–30]. This is because most of the existing studies have focused on enhancing the Li\(^+\) diffusion within LPBs, and have not adequately considered the importance of a rapid electron transfer for augmenting the LPB performance. Recently, considerable improvements in electrochemical performances of LIBs have been observed by using electrically modified electrodes as conducting additives, including graphene (G) sheets and/or carbon nanotubes (CNT) [31–35]. Further, it has been well established that such electrical conductors can improve the electron transfer that occurs from a current collector to the active materials of the composite electrodes [36, 37]. Furthermore, composite electrodes comprising a mixture of structurally different conducting additives have been observed to exhibit even more advantages; in particular, a smaller conducting additive can provide an effective electrical contact whereas a larger conducting additive can enhance the ionic diffusion [38]. However, excessive augmentations in the contents of such conducting additives can lead to an inhomogeneous slurry mixture and a poor adhesion between electrode materials, which in turn degrades battery performance.

In this study, a novel composite electrode was fabricated and the effect of various conducting additives on the performance of LPBs was investigated for the first time. Homogeneously well dispersed G, CNT, and a mixture of G and CNT (GCNT) solutions were prepared and directly utilized for fabrication of the LFP composite electrode. Subsequently, the effects of the conducting filler type and its content were systematically investigated along with the influence of the loading density of the composite electrode on the rate capabilities of LPBs. This investigation discovered that conducting fillers can effectively improve the rate capability of LFP composite electrodes. In particular, 1 wt\% GCNT was observed to produce excellent synergistic effects within the composite electrode, which effectively solved the issue of the poor rate capability of the LFP composite electrode even when the loading densities were augmented.

2. Experimental

2.1. Materials

Graphene platelets (G, N002–PDR) and multi-walled carbon nanotubes (MWCNT) were purchased from Angstron Materials and Hanwha Chemical, respectively. Poly(ethylene glycol) dimethyl ether (PEGDME, Mn \(\approx\) 500) was obtained from Sigma-Aldrich. The moisture level was reduced to less than 10 ppm by drying under vacuum at 80 \(^\circ\)C and using molecular sieves (4 Å) before use. Bisphenol-A ethoxylate diacrylate (BPh-A, Mn \(\approx\) 688) and N-methyl-2-pyrrolidone (NMP) were also purchased from Sigma-Aldrich. t-Butyl peroxypivalate (t-BPP) was obtained from Seki Arkema Co. for use as an initiator and was kept in a refrigerator before use. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was purchased from Sigma-Aldrich and dried in a vacuum oven at 120 \(^\circ\)C before use. Lithium iron phosphate (LFP) powder was obtained from Hanwha Chemical in Korea and polyvinylidene fluoride (PVDF, Kynar Flex® 2851) was provided by Arkema.
2.2. Preparation of CNT, G, and GCNT solutions
The CNT, G, and GCNT solutions were obtained by uniformly dispersing the respective fillers in NMP. Typically, 5 mg of CNT or 10 mg of G was dispersed in 2.4 ml of NMP by using ultra-sonication (VC500, Sonics & Materials, Inc.) for five hours. The resulting dispersion was then mixed further using a vortex mixer (Maxi Mix II, Thermolyne) for 15 min. Concentrations of up to 2.08 mg ml\(^{-1}\) for CNT solutions and 4.17 mg ml\(^{-1}\) for G solutions could be obtained by following this experimental method. In order to prepare CNT or G solutions with higher concentrations, the mixed solutions were vacuum dried to remove NMP. A GCNT (G : CNT = 1 : 1 in wt.) solution was obtained by mixing the same amount of G and CNT solutions. The NMP-based solution containing conducting carbons (G, CNT, or GCNT) was directly applied as a solvent for fabricating the composite electrodes.

2.3. Preparation of solid polymer electrolyte (SPE)
The SPE was prepared by thermal cross-linking a precursor solution using an initiator (t-BPP); the solution contained a cross-linker (BPh-A), plasticizer (PEGDME), and Li salt (LiTFSI). First, LiTFSI was completely dissolved in a PEGDME and BPh-A mixed solution by using magnetic stirring. The ratio between PEGDME and BPh-A was fixed at 8:2 by weight; subsequently, the concentration of the Li salt was adjusted to obtain an [EO]/[Li\(^{+}\)] molar ratio of 20. t-BPP at 1 wt% with respect to the BPh-A that was mixed in the precursor solution as an initiator before use.

2.4. Characterizations
A thermogravimetric analysis (TGA) curve was obtained using a thermogravimetric analyzer (Q500, TA Instruments) under a N\(_2\) atmosphere to analyze the thermal stability of the SPE. Differential scanning calorimetry (DSC) was carried out by using a differential scanning calorimeter (Thermo plus EVO II, Rigaku) to determine the glass transition temperature \((T_g)\) of the SPE.

2.5. Electrochemical characterizations
The ionic conductivity measurement was carried out by coating the polymer electrolyte onto a custom-built cell comprised of slide glass and pre-patterned indium tin oxide (ITO) glass with a gap of 100 \(\mu\)m [30]. The ionic conductivity was measured by electrochemical impedance spectroscopy (EIS) using an electrochemical impedance analyzer (IM6e, Zahner-elektrik) in a temperature range of \(-20^\circ\)C to \(100^\circ\)C. The temperature was controlled using a programmable oven. The electrochemical stability of the SPE was measured by linear sweep voltammetry (LSV) using a potentiostat (VMP3, Biologic) between 2 and 6 V versus (versus Li/Li\(^{+}\)) at a scan rate of 10 mV s\(^{-1}\). The two-electrode system consisted of a stainless steel plate (0.125 mm-thick, Hohsen Co.), working electrode, a microporous non-woven separator soaked with SPE precursor solution, and a lithium metal foil (Honjo metal) for the counter and reference electrodes; this system was assembled in a CR2032 coin-type cell for the LSV tests. After the assembly, the cells left for at least 30 min for penetrating the SPE precursor solution into pores within the composite electrode, and were placed in an oven at 90 \(^\circ\)C for 30 min to enable the thermal cross-linking of the SPE precursor solution and then cooled at room temperature.

To evaluate the electrochemical performance of LPBs, CR2032 coin-type cells were assembled, which consisted of the LFP composite cathode, a microporous non-woven separator soaked with SPE precursor solution, and a Li foil anode. The control LFP composite cathode was prepared by casting a slurry containing 70 wt% of LFP, 8 wt% of super-P carbon black, and 22 wt% of the polymer electrolyte (PE) binder in NMP onto an Al current collector, which was then dried in a vacuum oven at 120 \(^\circ\)C for 24 h. The PE binder consisted of PEGDME, PVDF, and LiTFSI. The fabrication process for composite cathodes modified with conductive carbon was the same as that used for the control composite electrode, except that a certain amount of super-P was replaced with CNT, G, or GCNT. Electrochemical performances in terms of charge-discharge cycles were analyzed using a battery tester (TOSCAT-3100, TOYO SYSTEM USA Inc.).

3. Results and discussion
To fabricate composite electrodes containing various conducting additives, a series of CNT, G, and GCNT solutions were prepared by uniformly dispersing the respective fillers in NMP. Generally, strong van der Waals forces between each individual CNT and pi–pi stacking interactions between each individual G sheet lead to the formation of an inhomogeneous slurry dispersion, which hinders the formation of a conducting network in the composite electrode [39, 40]. The introduction of functional groups on the surface of fillers or stabilizers has recently been applied to prevent the agglomeration between the CNTs or graphene sheets [41–43]. While these modifications produce a uniform dispersion, the functional groups or stabilizers inevitably reduce the electrical conductivity of the fillers; this eventually leads to a negative impact on electrochemical performance. The
Homogeneously well dispersed CNT, G, and GCNT in the NMP solutions were prepared in a simple and cost-effective way without affecting the electrical conductivity; this was achieved by using probe sonication and mechanical shaking, as shown in figure 1(a) (see the experimental section for further details). The CNT, G and GCNT suspensions were compatible with other electrode materials, which resulted in the formation of uniform composite electrodes on an Al-foil current collector (figure 1(b)). These conducting fillers are believed to enhance the penetration of the electrolyte, shorten the Li\textsuperscript{+} diffusion distances, and provide electrical conducting channels throughout the electrode \[44\]. Moreover, these conducting fillers are also directly related to the increase in the loading density of electrodes. The formation of effective conducting channels is able to reduce the number of electrical conductors required to reach the percolation threshold.

The SPE was fabricated via \textit{in situ} crosslinking polymerization of a cross–linker by using acryloyl groups to form a network structure in the presence of EO-containing plasticizer and Li salt; this led to the formation of a semi-interpenetrating polymer network (IPN). The glass transition temperature (\(T_g\)) of the SPE showed a \(T_g\) value of \(-73.7^\circ\)C (figure S1(a) is available online at stacks.iop.org/MRX/7/075504/mmedia in the supplementary information (SI)), which was significantly lower than the value reported for a pure PEO electrolyte (\(-65.2^\circ\)C) \[45\]. The lower \(T_g\) value of the SPE reflects the high mobility of the polymer chain and the resultant faster ionic transporting ability of the SPE \[45\]. The ionic conductivity of the SPE was determined to be \(5.2 \times 10^{-4}\) S cm\(^{-1}\) at room temperature (30°C) (figure S1(b) in the SI), which was significantly higher than other recently reported PEO-based SPEs \[46–49\]. The SPE exhibited an electrochemical stability window of up to 5.50 V (versus Li/Li\textsuperscript{+}) at room temperature (figure S1(c)), which was also higher than those of the previously reported SPEs based on polycrylates (4.5 V) \[50\], polysiloxane (5.2 V) \[51\], and polyurethane (5.35 V) \[52\]. This wide electrochemical stability window can fully cover the working ranges of most LIBs and potentially enhance the performance of LPBs by using the SPE at relatively high potentials. Moreover, the SPE displayed thermal stability at temperatures above 200 \(^\circ\)C (figure S1(d) in the SI), which indicates that the SPE has a significantly higher thermal stability as compared to those of conventional liquid electrolytes \[53, 54\]. Li\textsuperscript{+} transference number of the SPE used in the present study was calculated using the Bruce–Vincent equation at room temperature (figure S2 and table S1 in the SI) \[55\]. Theoretically predicted Li\textsuperscript{+} transference number is less than 0.5 \[56\], and the most of PEO:LiTFSI electrolyte system showed Li\textsuperscript{+} transference number in the range of 0.1–0.5 \[57\]. Hence the calculated SPE Li\textsuperscript{+} transference number of 0.41 is reasonable.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Schematic illustrations for (a) the preparation of CNT and G solutions, and (b) the fabrication of a composite electrode by using CNT, G, or GCNT solutions.}
\end{figure}
The electrochemical performance of an LPB using the control LFP composite electrode with a loading density of 1.3 mg cm$^{-2}$ was preferentially analyzed in the presence of the SPE with a galvanostatic charge-discharge between 2.5 and 4.2 V (versus Li/Li$^+$) (figure 2(a)). The observance of typical plateaus at approximately 3.45 V (versus Li/Li$^+$) clearly represents the characteristics of a Fe$^{3+}$/Fe$^{2+}$ redox couple for LFP [23, 46]. The gradual increase in the polarization between the charge-discharge cycles as the C-rate increases was primarily due to the current density associated with the increasing resistance of the composite electrode. The average specific capacities at 0.2 C, 1 C and 5 C were 150.4 mAh g$^{-1}$, 130.3 mAh g$^{-1}$ and 36.1 mAh g$^{-1}$, respectively (figure S2 in the SI). The relatively high specific capacity and good rate capability of the LPB could be due to the insertion of a PE binder in the composite electrode and the high ionic conductivity of the SPE, respectively. As mentioned above, PEGDME containing PE binder was introduced within the LFP composite electrode, and SPE precursor solution could penetrate the pores within the composite electrode before the thermal cross-linking. Which could provide a direct pathway for the Li$^+$ conduction within the whole LPB cell, reducing interfacial resistance between the SPE and the composite electrode, and result in the relatively high specific capacity of the LPB cell [30, 58]. While the LPB showed good rate capability with a relatively low electrode loading density of 1.3 mg cm$^{-2}$, it dramatically degraded as the loading density was increased (figure 2(b)). The LPB cell with a loading density of 1.3 mg cm$^{-2}$ could maintain over 20% capacity at high 5 C. In comparison, the capacity retention of a cell with a loading density of 4.4 mg cm$^{-2}$ was limited to less than 5% even at 1 C, based on the average specific capacity at 0.2 C. The LPB cells had several features, which allowed for an expedited Li$^+$ diffusion within the whole cell, namely: (i) the use of SPE with relatively high Li$^+$ conductivity; (ii) the use of a composite electrode containing Li$^+$ conducting PE binder; and (iii) adopting in situ polymerization of the SPE precursor solution after cell fabrication to reduce interfacial contact with electrode materials. The deprived rate capability of the LPB cells at higher loading densities was therefore thought to be due to a deteriorated electrical contact resistance, rather than Li$^+$ conduction.

In order to construct an effective conducting network to reduce the electrical resistance, conducting fillers such as CNT, G and GCNT were introduced into the LFP composite electrode. Firstly, the effect of filler contents on the performance of LPBs was investigated using different amounts of CNT with identical loading densities of 1.3 mg cm$^{-2}$. Figure 3(a) shows the galvanostatic charge-discharge potential curves of LPBs using the LFP/CNT composite electrodes with various amounts of CNT. The entire LFP/CNT composite electrodes displayed a significant improvement in specific capacity at relatively high C-rates in comparison to those of the control LFP composite electrode. The gaps between each plot are clearly discernible at relatively high C-rates. It is reasonable to conclude that the high electrical conductivity of CNT effectively contributed to the rapid electron transport at high C-rates and thereby increased the specific capacity of the LFP/CNT composite electrodes. To select the optimum amount of conducting fillers, the average specific capacities of the electrodes at each C-rate were calculated and plotted against CNT contents. Figure 3(b) shows the average specific capacities of LPBs using the LFP/CNT composite electrodes with different amounts of CNT at the various C-rates tested in this study. A clear correlation was observed between increases in the average specific capacities and CNT content, with the average specific capacities stabilizing at a CNT content of approximately 1 wt%. A CNT content of 1 wt% was considered to be a saturation limit for obtaining maximum specific capacity and this loading amount was used in further experiments.

The effect of various conducting fillers on the rate capability of LPB cells at a fixed CNT content of 1 wt% was then investigated. Composite electrodes modified with 1 wt% of G, CNT or GCNT were prepared and their
electrochemical performance was compared with the control LFP composite electrode at an identical loading density of 2.2 mg cm\(^{-2}\) (figure 4). All the conducting fillers were observed to provide an improvement of specific capacity at higher C-rates. The capacity retention at 2 C for the LPB cells using the control LFP, LFP/G, LFP/CNT and LFP/GCNT composite electrodes were 9.4%, 36.8%, 20.8%, and 43.1%, respectively. The higher rate capability of the cell using the LFP/GCNT composite electrode can be attributed to the synergistic effect of G and CNT with different structures improving the electrical contact [38].

Figure 5 presents a comparison of the electrochemical performance of LPB cells using the control LFP and LFP/GCNT composite electrodes with an elevated loading density of 3.2 mg cm\(^{-2}\). Both LPB cells displayed a gradual increase in overpotentials and a decrease in specific capacities as the C-rate increased. Nonetheless, the degree of overpotential increase and capacity decrease for the LPB cell using the LFP/GCNT composite electrode was substantially less than those observed for the cell using the control LFP composite electrode (figures 5(a) and (b)). The average specific capacity of approximately 146 mAh g\(^{-1}\) at 0.2 C for the cell using the control LFP composite electrode was markedly reduced to approximately 11 mAh g\(^{-1}\) at 1 C. Comparatively, the decrease in the average capacity for the cell using the LFP/GCNT composite electrode from approximately 158 mAh g\(^{-1}\) at 0.2 C to 99 mAh g\(^{-1}\) at 1 C (figure 5(c)) was relatively small. The cell using the control LFP and LFP/GCNT composite electrodes retained 7.6% and 72% of their capacity respectively at 1 C (figure S3 in the SI).

During the subsequent tests at 0.2 C, the cell using the control LFP composite electrode retrieved almost the whole capacity (>99%), whereas the cell using the LFP/GCNT composite electrode displayed even higher capacities (>102%). The significantly improved electrochemical performance of the LFP/GCNT composite electrode can be attributed to the enhanced electrical contact and reduced resistance resulting from the
uniformly distributed GCNT conducting fillers within the composite electrode. The electrochemical impedance spectroscopy (EIS) result acquired from the cell using the LFP/GCNT composite electrode displayed a much lower charge resistance in comparison to that of the LFP control composite electrode. This result confirms that GCNT effectively increased the electrical conductivity in the composite electrode and led to diminished charge transport resistance. Importantly, these results also clearly indicate that both Li\(^+\) diffusion and electrical conduction in a composite electrode are extremely important to achieve high performance of LPBs.

A similar tendency was also observed when the loading density of composite electrodes was further raised to 4.4 mg cm\(^{-2}\) (figure S4 in the SI). While the LPB cell using the control LFP composite electrode only delivered a specific capacity of approximately 3.5 mAh g\(^{-1}\), the specific capacity of the cell using the LFP/GCNT composite electrode was 66.6 mAh g\(^{-1}\) at 1 C. Figure 6 shows plots of capacity retention as a function of C-rate for LPB cells using the control LFP and LFP/GCNT composite electrodes with different loading densities to clarify the effect of GCNT on the rate capability of cells. This shows that the increase in the loading density and C-rate inevitably led to a deterioration in the specific capacity of LPB cells using both composite electrodes. However, the capacity retention and rate capability were significantly improved for the LFP/GCNT composite electrode for all loading densities used in this study, as compared to those of the control LFP composite electrode. Figure 6 clearly demonstrates that GCNT enhances the electrical conductivity of the composite electrode, thereby improving the electrochemical performance of the LPB.

The cycle stability at room temperature of the LPB cell using the composite electrode was also investigated. Figure S5 in the SI shows plots of the specific capacity of the LPB cell using the LFP/GCNT composite electrode with a loading density of 2.2 mg cm\(^{-2}\) at 0.5 C. After the cell achieved a specific capacity of 127.8 mAh g\(^{-1}\) during the initial cycle, this value slightly increased for approximately up to 10 cycles, which was considered to be due to the augmented electrolyte wetting of the composite electrode. The cell reached the maximum specific capacity of 132.3 mAh g\(^{-1}\), which was then gradually decreased during the subsequent cycles. After 100 repetitive charge-discharge cycles, the cell retained 94.5\% (120.8 mAh g\(^{-1}\)) of the initial capacity. This result, which was obtained at room temperature, was quite outstanding given that the majority of the LPB cells were being tested at elevated temperatures (table S2 in the SI) [23–25, 28, 29, 46, 47, 49]. The superior performance of the LPB using the LFP/GCNT composite electrode was attributable to the high Li\(^+\) conductivity of the SPE at room temperature, a lowered ionic resistance due to the adoption of PE binder and in situ polymerization, and an enhanced electrical conductivity obtained by introducing G and CNT conducting fillers within the composite electrode.

![Figure 5. Galvanostatic charge-discharge potential curves of LPB cells using the (a) control LFP, and (b) LFP/GCNT composite electrodes with an identical loading density of 3.2 mg cm\(^{-2}\) at various C-rates. (c) Plots of specific capacities at various C-rates, and (d) Nyquist plots for the LPB cells using the control LFP and LFP/GCNT composite electrodes.](image)
4. Conclusion

This study demonstrated the successful preparation of LFP composite electrodes, which were modified with various conducting carbons. LPBs using the composite electrodes together with in situ semi-IPN SPE were fabricated and their electrochemical performance was investigated. It was found that the rate capability decay of the composite electrode at higher loading densities or elevated C-rates was directly attributable to the increased charge transfer resistance of the composite electrode. Furthermore, the modification of the composite electrode with conducting fillers could effectively provide rapid electron transport pathways. Importantly, the LFP/GCNT composite electrode with 1 wt% of GCNT displayed the ability to reduce the charge transport resistance, thereby improving the electrochemical performance of the LPB using the electrode. The results obtained in this study clearly demonstrate that the electrical conduction facilitated within a composite electrode, along with an expedited Li$^+$ diffusion, is extremely important for the performance of LPBs.

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Figure 6. Plots of capacity retention vs. C-rate for LPB cells using the control LFP and LFP/GCNT composite electrodes with different loading densities.
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