INCLUSION OF POLYVINYLEDENE FLUORIDE POLYMER AS BINDING AGENT FOR GRAPHITE AND LICOO₂ GRANULES

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ABSTRACT

In this research, the technique to deposit Polyvinyledene fluoride (PVDF) polymeric binder on the surface of graphite (anode) and LiCoO₂ (cathode) granules, through dissolution and solid precipitation method were developed. The binder material needed to be added into the electrode granules to ensure good interfacial contact which is required to improve ionic diffusion across the boundaries. The process utilized organic solvent dimethylsulfoxide (DMSO) to dissolve the PVDF at 5-10% w/v under constant heating (80°C). Once dissolved, the solution was then mixed with graphite or LiCoO₂ granules to make up final concentrations of 3-5% w/w PVDF. The organic solvent was then evaporated using two stages of drying at 90°C and 110°C. The final stage of drying was performed under vacuum and ceased when 10⁻³ g difference between weighing was achieved. The results were then subjected to SEM coupled with EDS studies. The SEM results for LiCoO₂ clearly showed that the PVDF have precipitated either as nano size particles throughout the surface of granules, or as fiber like structures that covered the entire surface of LiCoO₂ granules in the more concentrated area. As for graphite, however, the presence of PVDF was less obvious. The presence of PVDF could not be seen clearly at the magnification used in this study. In spite of this, in both cases, the EDS analysis clearly indicated the presence of the element fluorine (F) on the surface (0.677 keV) which was the signature of the presence of PVDF. Furthermore, following the inclusion of PVDF, both graphite and LiCoO₂ granules could be easily made into pellet with good physical integrity. Plans to investigate the effects of PVDF on ionic transport have been laid out. Moreover, the effects of this PVDF inclusion into the RF sputtering in the construction of thin film micro-battery would also be studied.

Keywords: LiCoO₂, graphite, electrode, PVDF, SEM, EDS

INTRODUCTION

As part of the current project in the utilization of the new glass base LiPO₃ electrolyte for the construction of Li ions rechargeable battery, graphite is used as the anode material, while LiCoO₂ is used as the cathode material (Kartini 2008, Putra 2008, Suminta 2007). In the process, the Li⁺ ions are shuttling to be intercalated and de-intercalated between CoO₂ and graphite matrix during the charging/discharging process [Sukla 2008, Hua 2007, Nugraha 2008]. The graphite particles and the granules of LiCoO₂ need to be made into pellets. This is required for the construction of coin type battery prototypes, as well as the pellets required for sputtering target that is needed in the construction of thin film all-solid-state micro-
battery [Dudney 2008, Kawamura 2005]. The pelletization procedure, however, was hampered by the fact that, particularly; the LiCoO₂ could not be made into pellets due to the lack of cohesion forces between the particles. To some extent, the graphite particles also showed some lack of cohesion problem despite the fact that was not as serious as LiCoO₂. To overcome this problem, polyvinylidene-fluoride (PVDF) polymer was used as the binder material. It was hoped that through the inclusion of PVDF as binder material, pellets with good cohesion of both LiCoO₂ and graphite could be made. Moreover, it was also hoped that the electrochemical properties of the pellets as electrodes would be improved. This could be expected since the porous nature PVDF [Mago 2008] might provide bridges for the Li⁺ ions during its movement between the granules of LiCoO₂ or graphite. The presence of PVDF at the inter-granular boundaries would fill in the void spaces which otherwise would be impossible for Li⁺ ions to pass through.

In this research, methods to deposit PVDF polymeric binder on the surface of LiCoO₂ and graphite were developed. The methods for the inclusion of PVDF must be capable of depositing small size precipitates of PVDF on the surface of the LiCoO₂ and graphite particles. Moreover, the technique must also allow relatively even distribution of PVDF solid precipitates across the surfaces of all particles. Such condition would optimize the cohesion of the pellets, as well as optimize the electrochemical properties of the pellets one they are made into components of the batteries. As noted previously, the PVDF is also expected to provide bridges for Li⁺ ions to pass regions which would otherwise be non-passable void spaces. The results of the deposition of precipitate were then studied by using SEM coupled with EDS analysis. Moreover, the pellets of the LiCoO₂ as well as graphite were attempted to be made for later use in coin type battery prototype and micro battery sputtering targets.

**MATERIALS AND METHODS**

PVDF ([C₂H₂F₂]ₙ) in the form of pellets and LiCoO₂ granules used in this research were obtained from Aldrich, while the graphite electrode was obtained from Merck. To dissolve the polymeric PVDF, dimethylsulfoxide or DMSO (Merck, analytical grade) was used. In the process, the PVDF was dissolved at slightly elevated temperatures of 70°C to 80°C with slow mixing using magnetic stirrer. This was necessary to provide energy to speed up the dissolution of PVDF pellets in the solvent. Care should be taken to remove vapor of the DMSO from the headspace of the mixing vessel to reduce possibility of attaining DMSO’s flash point. The procedure must, therefore, be carried out in a well ventilated area such as inside a fume hood. The solution was made such that the concentration of PVDF in the solvent was 5% to 10% w/v. This solution was then ready for uses.

To include PVDF binder in the LiCoO₂ or graphite granules, the solution made above was mixed with LiCoO₂ or graphite. A measured volume of PVDF solution was then mixed with a known amount of LiCoO₂ or graphite such that the concentration of PVDF in the final dried product was 3% or 5% w/w. This amount should suffice to provide binding force for good cohesive pellets of electrode. In the process, the PVDF solution was mixed with the granules of electrode while the DMSO solvent was evaporated slowly at a temperature of 90°C. Faster evaporation of DMSO can be effected at an increased temperature if necessary since the boiling point of DMSO is 180°C. It is important that stirring is done on the mixture during the drying stage to ensure a relatively homogeneous distribution of PVDF. Once most of the DMSO is evaporated, a final drying stage inside a vacuum chamber was carried out at a temperature of 110°C. This is done to ensure more complete loss of the DMSO which is not wanted in the final product of LiCoO₂ pellet. Drying was stopped when the difference between two consecutive weighing was in the order of 10⁻³ g or less. The result of the drying stage was then analyzed using SEM (JEOL) coupled with EDS to confirm the presence of
PVDF in the granule of electrode. Moreover, the distribution of PVDF precipitates on the surface of the granules of LiCoO$_2$ or graphite could also be observed.

RESULTS AND DISCUSSION

**PVDF in LiCoO$_2$**

Following the PVDF inclusion, the granules of the LiCoO$_2$ were subjected to SEM and EDS analysis before and after the inclusion of binder. The concentration of PVDF used in the result below was 3% w/w PVDF in LiCoO$_2$.

It is noted that the granules of LiCoO$_2$ seemed to come in various shapes and sizes. The measurement of each granule appeared to vary between approximately 1 µm to slightly larger than 10 µm. The presence of PVDF binder can be seen in the figure (Figure 1 and Figure 2) either as dotted precipitates which appeared to be in nano-meter sizes that are scattered on the surface of the granules, or in the more concentrated region, as web or fiber-like material that covers an entire granule or connecting between granules surfaces. It is clear that the nano-dot precipitates would be the preferable type of PVDF deposits, since this way, the PVDF tended to be deposited more homogeneously throughout the surface of the granules. This should be expected to yield more uniform physical properties and electrochemical properties of the made up electrode pellets. It is possible that more aggressive stirring during the entire time of DMSO solvent evaporation was required. It is noted that when most of the solvent had been evaporated, the mixture behaved more like a paste and, hence, it was more difficult to stir. As a result, less than ideal distribution of the PVDF could be observed as shown in the figure. Despite the still non-homogeneous nature of the spread of the PVDF, the binder material was successful in binding the LiCoO$_2$ and the graphite into pellets with sufficient cohesion for the purpose of testing of the coin battery (1cm diameter), as well as to be utilized as sputtering target (2.5cm diameter). Its effect on the electrochemical properties of the LiCoO$_2$ however is not yet studied.

![Figure 1: SEM results of PVDF inclusion in LiCoO$_2$](image1.png)

![Figure 2: Deposits of PVDF on the surface of LiCoO$_2$](image2.png)
Furthermore, the EDS results of the LiCoO$_2$ materials are also shown in Figure 3. It can be seen that the presence of Fluorine which is one of the components of PVDF was detected at 0.677 keV. It should also be noted, however, that the concentration reported here is the surface concentration of PVDF (8.75% w/w). Hence, it does not reflect the overall % mass fraction of the PVDF in LiCoO$_2$. As described previously, the concentration of PVDF in the system was set at 3% w/w.

**PVDF in Graphite**

Some results of SEM and EDS results of PVDF inclusion on graphite surface are also described here. The magnification was set at 1000x and 2000x. At this point it is difficult to confirm the presence of PVDF by visual inspection alone. Likely, stronger magnification is required as it was shown for LiCoO$_2$ which had been carried out at magnification of 1000x and 5000x. The confirmation of the presence of PVDF, however, could be seen from the result of the EDS analysis which detected the presence of fluorine on the surface of graphite at 0.677 keV, at a concentration of 7.46% w/w. As before, this concentration is only relevant to concentration of PVDF deposited on the surface, and hence, it does not reflect the bulk concentration of fluorine in graphite matrix.

![Figure 4: SEM results of PVDF inclusion in graphite](image1)

![Figure 3: EDS Result of PVDF inclusion in LiCoO$_2$](image2)
In spite of this, the PVDF presence at 5% w/w was found to be successful in binding the graphite material into a cohesive pellet. In the next segment of the research the electrochemical properties of the pellets for both LiCoO₂ and graphite, after the inclusion of PVDF, would be studied as well. Moreover, this would also be accompanied by the studies involving XRD to study their crystal structures.

CONCLUSIONS

The technique to deposit Polyvinylidenefluoride (PVDF) polymeric binder on the surface of graphite (anode) and LiCoO₂ (cathode) granules, through dissolution and solid precipitation method have been developed. The binder was dissolved in dimethylsulfoxide (DMSO) at 5-10% w/v under constant heating (80°C). Once dissolved, the solution was then mixed with graphite or LiCoO₂ granules to make up final concentrations of 3-5% w/w PVDF. The organic solvent was then evaporated using two stages of drying at 90°C and at 110°C. The SEM results for LiCoO₂ clearly showed that the PVDF have precipitated either as nano size particles throughout the surface of granules, or as fiber like structures that covered the entire surface of LiCoO₂ granules in the more concentrated area. As for graphite, however, the presence of PVDF was less obvious. The presence of PVDF could not be seen clearly at the magnification used in this study. The EDS analysis clearly indicated the presence of the element fluorine (F) on the surface (0.677 keV) which was the signature of the presence of PVDF. Furthermore, following the inclusion of PVDF, both graphite and LiCoO₂ granules could be easily made into pellet with good physical integrity.

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