

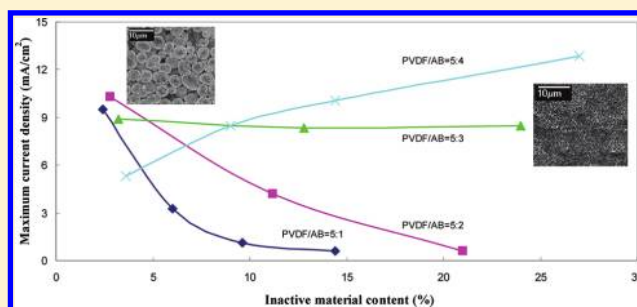
Cooperation between Active Material, Polymeric Binder and Conductive Carbon Additive in Lithium Ion Battery Cathode

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ABSTRACT: A lithium ion battery electrode is a composite of active material, polymeric binder, and conductive carbon additive(s). Cooperation among the different components plays a subtle and important role in determining the physical and electrochemical properties of the electrode. In this study, the physical and electrochemical properties of a $\text{Li-Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode were investigated as a function of the electrode compositions. The electrode conductivity, porosity, specific capacity, first Coulombic efficiency, and rate capability were found significantly affected by the polyvinylidene difluoride (PVDF)-to-acetylene black (AB) ratio and the total inactive material amount. The electronic conductivity of the laminate does not so much decide the rate performance of the electrode as it is generally believed. The rate capability of the electrode is enhanced by an increase in the total inactive material content at a PVDF/AB ratio of 5:4, whereas it is deteriorated by increasing the total inactive material content at PVDF/AB ratios of 5:1 and 5:2. At a PVDF/AB ratio of 5:3, the rate performance is not considerably affected by the inactive material content. The result is explained by the competition between the ion-blocking effect of PVDF binder and the electronic conducting effect of the AB additive. A long-term cycling experiment shows the mechanical integrity of the laminate is important for the durability of the composite electrode.



1. INTRODUCTION

Electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs) call for high energy density at moderate/high power levels. To meet the aggressive requirements of lithium batteries for EV and PHEV purposes, much effort has been made in the research and development of high-energy electrode materials. Because of the cathode-limited property of lithium ion cells, new cathode materials of high potential and high capacity have been highlighted for many years; however, less attention is paid to the engineering approaches of the cathode laminate; for instance, the optimization of electrode compositions, structure, porosity, and so on.^{1–4}

Typically, a lithium ion battery cathode is a composite consisting of agglomerated primary particles of active intercalation compounds (called secondary particles) and inactive materials coated and calendered onto Al current collectors. The inactive materials are referred to as polymeric binder and conductive additive(s). The active material acts as the lithium reservoir in the electrode, the binder plays the role of binding the active materials and the conductive additive together and adherent to the current collector, and the conductive additive contributes to an increase in the electronic conductivity of the laminate. Cooperation between the different components contributes to an electrochemical property enhancement of the electrode by placing the electrode particles closer together and making the laminate more conductive. However, it should be noted that the role of each component is

also restrained by the others.^{5,6} For example, the electronic conductivity resulting from a carbon additive can be brought down by the presence of a more nonconductive binder and oxide active material, and the close contact between active material particles with the help of a binder can be spoiled by the appearance of more nanocarbon additive, etc. From this point of view, the optimization of electrode compositions is crucial for fabrication of high-quality electrodes for EV or PHEV purposes.

Although there are some reports in the literature regarding the effects of electrode composition on electrochemical performance, the results obtained are always very specific. Many fundamental scientific issues relating to the cooperation among different cathode elements remains a matter of conjecture. Comprehensive understanding of how the cooperation among electrode elements affects the physical and electrochemical properties of the laminate is of great significance for designing high-quality electrodes to meet the requirements of EVs and PHEVs.

The current work systematically demonstrates the physical and electrochemical properties of a $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode laminate as a function of the electrode compositions. $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ was chosen as the cathode material

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because of its high specific energy and specific power. This cathode material is very promising for EV and PHEV applications.^{7,8} Polyvinylidene difluoride (PVDF) and acetylene black (AB) were chosen as the polymeric binder and conductive carbon, respectively, because they are still premium choices for cathodes in commercial lithium ion cells.^{9,10} The effects of the PVDF/AB ratio and the total inactive material content on the electrode's porosity, conductivity, first Coulombic efficiency, and rate capability were mapped out. The results are interpreted by the competition between the ion-blocking effect of PVDF and the electronic conducting effect of AB.

2. EXPERIMENTAL SECTION

The active cathode material, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, with a mean particle size of 6 μm , was obtained from Toda, Japan. Battery-grade AB with an average particle size of 40 nm was acquired from Denka Singapore Private Ltd. PVDF (KF1100) binder was supplied by Kureha, Japan. *N*-Methylpyrrolidone (NMP) was purchased from Aldrich Chemical Company.

Premixed PVDF/AB/NMP mixtures were made by dissolving a certain amount of PVDF into anhydrous NMP solvent. A calculated amount of AB was then dispersed in the PVDF polymer solution. To ensure thorough mixing of the AB nanoparticle into the polymer solution, a Branson 450 sonicator equipped with a solid horn was used. The sonic dispersion process took ~ 30 min until a very uniform mixture was formed. The PVDF/AB ratio was varied from 5:0 to 5:7 by weight. The well-mixed PVDF/AB/NMP mixture was cast onto copper foil using the doctor blade method and thoroughly dried at 120 $^{\circ}\text{C}$ under vacuum.

Electrode slurries were prepared by adding the targeted amount of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ active material to a certain amount of the premixed AB/PVDF/NMP mixture. The slurry was homogenized by using a Polytron PT10-3S homogenizer at 4000 rpm for 15 min until a viscous and uniform slurry was acquired. Electrode laminates were prepared by casting the slurries onto aluminum foil by the doctor blade method. By varying the height of the blade, all the electrode films were cast to have approximately the same loading of active material (around 11.5 mg/cm^2) to eliminate the thickness effect on the electrochemical performance of the electrode. All the electrode laminates were dried at 130 $^{\circ}\text{C}$ for 10 h under vacuum before use. Surface morphologies of the electrode films containing the same PVDF/AB ratio of 5:3 and different inactive material contents were imaged by field-emission scanning electron microscopy (FESEM) with a JEOL FESEM set at 5 kV.

Conductivities of PVDF/AB films and the composite electrode laminates were measured using a four-point probe. The PVDF/AB films were removed from the foil, and the electrode laminates were peeled from the aluminum foil before testing. The dc conductivity measurement was performed using a Jandel equal-distance linear four-point probe apparatus with a Solartron 1286 Electrochemical Interface and a CorrWare software package.

The breaking stress of the PVDF/AB films was measured by using a Chatillon TCD225 force measurement system. A stretching speed of 0.0001 in./s was applied in this study. Determination for each sample was repeated five times. The breaking stress of the laminate is defined as the quotient of the maximum force applied onto the film until it breaks and the

section area of the laminate. It is calculated from the following equation:

$$\text{breaking stress} = (\text{force}_{\text{max}})/(\text{width} \times \text{thickness}) \quad (1)$$

$\text{Force}_{\text{max}}$ in the equation refers to the maximum force applied to the film when it breaks.

The porosity of the electrode laminate was calculated taking into account of the true density of the mix obtained from X-ray measurements,

$$\text{porosity} = (L - W(C1/D1 + C2/D2 + C3/D3))/L \quad (2)$$

where L is the real thickness of the electrode laminate (without Al foil); W is the weight of the laminate per area; $C1$, $C2$, and $C3$ are the percentage of active material, PVDF binder, and acetylene black within the electrode laminate; and $D1$, $D2$, and $D3$ are the true density for $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, PVDF, and acetylene black, respectively. The true densities for $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ active material, PVDF, and AB are 4.73, 1.78, and 1.95 g/cm^3 , respectively. Porosities of the free-standing electrodes were calculated and compressed to 35% porosity using a calender machine with a continuously adjustable gap prior to electrochemical testing.

Half cells were fabricated with standard 2325 coin-cell hardware. The separator employed was a Celgard 2400. Lithium foil was used as the counter electrode. The electrolyte was 1 mol/dm^3 LiPF_6 /ethylene carbonate (EC) + diethyl carbonate (DEC) (1:1 by weight ratio) obtained from Novolyte. All cells were tested using a Maccor battery test cycler at 303 K in a Thermotron environmental chamber. Three formation cycles at C/10 charge and discharge were first applied. The upper cutoff voltage limit was set at 4.1 V, and the cell was held at this voltage until the current dropped to C/20. The discharge voltage limit was set at 3.0 V. The discharge capacity of each cell determined from the last formation cycle was used to estimate the C rate for all subsequent cycles. The rate performance test consisted of full discharges at rates of C/10, C/5, C/2, 1 C, 2 C, 5 C, 10 C, and 20 C. A charge of C/10 to 4.1 V preceded each discharge.

Full cells were assembled with the cathodes containing different inactive material contents at the same PVDF/AB ratio of 5:3 and mesocarbon microbeads (MCMB) anode. The MCMB anode consists of 88.8% active material, 8% PVDF, and 3.2% acetylene black. The capacity of the MCMB anode per area is slightly higher than that of the cathode to prevent lithium deposition. The separator and electrolyte employed are the same as those used in half cells. Ten formation cycles for the full cells were performed at C/24 to ensure the complete formation of the surface film for both cathode and anode. The charge voltage limit was set to 4.1 V, and the discharge voltage limit was 3.0 V vs Li. The last discharge capacity during the formation cycles was used to estimate the capacity of the cells. Long-term cycling of the full cells was carried out with a 1 C charge to 4.1 V and followed by 1 C discharge to 3.0 V for 600 cycles.

3. RESULTS AND DISCUSSION

3.1. The Cooperation between PVDF Binder and AB Additive in PVDF/AB Film. The electronic conductivities and mechanics of the PVDF/AB composites were determined to evaluate the cooperation between the PVDF and AB in the composite films. Electronic conductivity of the composite film

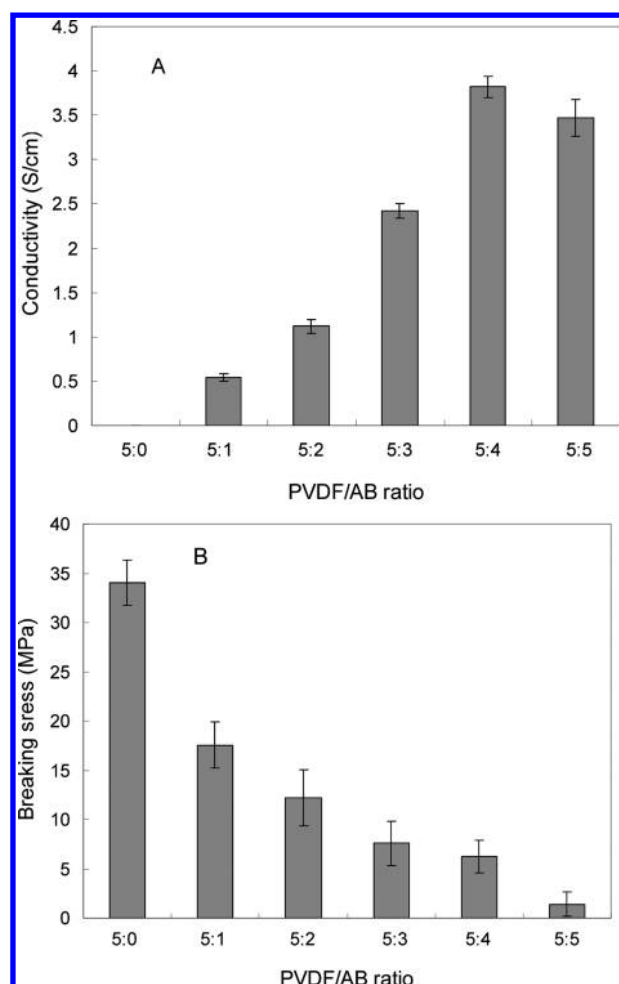


Figure 1. Electronic conductivity (A) and breaking stress (B) of the PVDF/AB composite film at different PVDF/AB ratios.

versus the PVDF/AB weight ratio is shown in Figure 1A. As expected, pure PVDF film is electronically insulating without the presence of acetylene black. An increase in the AB content brings about a significant enhancement of the electronic conductivity of the film, which results from the formation of conductive paths, that is, an acetylene black network.¹¹ A maximum conductivity of the composite was obtained at a PVDF/AB ratio of 5:4. The film conductivity starts to drop with a further increase in the AB content, which should be associated with the poor connectivity between the AB particles due to the shortage of the PVDF binder. At a high AB content, the binder is insufficient to maintain the conductive particles together as a network.

Figure 1B displays the mechanical property of the PVDF/AB film as a function of the PVDF/AB weight ratio. The strength of the composite is related mainly to the entanglement of PVDF chains. A pure PVDF film demonstrates the highest breaking stress, around 34 MPa, and the breaking stress is greatly decreased with an increase in the AB content. It shows that the entanglement between PVDF chains is spoiled by the presence of AB particles. When the AB fraction is equal to or higher than that of PVDF binder, the poor mechanical property of the PVDF/AB film implies the nanocarbon particles are not effectively held together due to the lack of binder. The mechanical failure of the composite film is consistent with the conductivity decline at the high AB content, as shown in Figure 1A.

Increasing the AB content to a PVDF/AB ratio of 5:4 contributes to a large increase in the electronic conductivity while the mechanical properties greatly deteriorate. A further increase in AB content brings about a conductivity decline due to the mechanical failure of the composite. Therefore, optimization of the PVDF/AB ratio is important for fabricating an electrode laminate of both high mechanical strength and high conductivity. For the chosen different PVDF/AB ratios in this study, the composite at a 5:0 ratio is nonconductive, which is not suitable for use with oxide cathode materials. On the other hand, the composites at 5:5 and 5:6 ratios suffer from extremely low mechanical strength and decreased conductivity, which have been proven not to be good recipes for use with $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ active material.¹ Therefore, a comprehensive electrochemical study of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes was carried out with various inactive materials contents at PVDF/AB ratios of 5:1, 5:2, 5:3, and 5:4, respectively.

3.2. Physical Properties of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Cathodes Containing Various Contents of Inactive Materials at Different PVDF/AB Ratios.

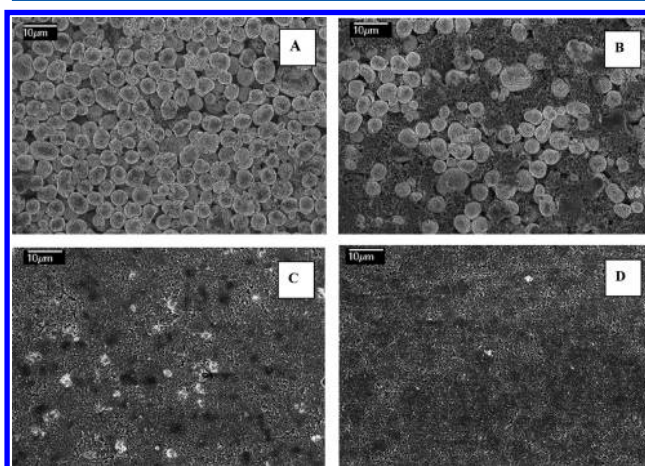


Figure 2. SEM images of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ composite electrodes containing different amounts of inactive materials at a fixed PVDF/AB ratio of 5:3. (A: 2% PVDF + 1.2% AB. B: 8% PVDF + 4.8% AB. C: 15% PVDF + 9% AB. D: 20% PVDF + 12% AB.)

SEM micrographs of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ composite electrodes containing different amounts of inactive materials at a fixed PVDF/AB ratio of 5:3. With 2% PVDF and 1.2% AB, the electrode is shown to be a stack of active material. Spherical $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ particles with an average particle size of 6 μm are observed. Nanocarbon agglomerates are not homogeneously dispersed in the electrode. This is because the nanocarbon particles easily flocculate as a result of their large surface area and high oil adsorption properties.¹² When the inactive material was increased to 8% PVDF and 4.8% AB, the nanocarbon agglomerates are still not evenly distributed; however, percolation of the nanocarbon particulates is developed. The conductive network is interconnected by particle-to-particle contacts; that is, continuous electronic paths are developed within the electrode from side to side. When the inactive material content is increased to 15% PVDF and 9% AB or even higher, the active material particles are seen immersed into the matrix of the PVDF/AB composite.

Figure 3 displays the variations of the electronic conductivity of the electrode laminate with total inactive material content at different PVDF/AB ratios. As expected, the electrode is not

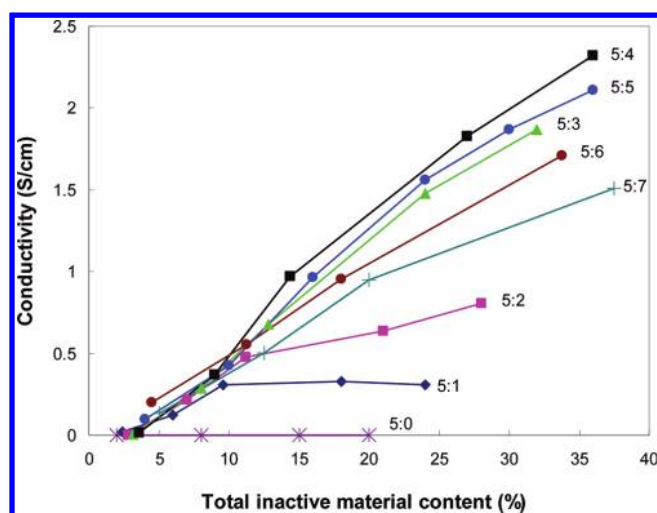


Figure 3. Variations of the electronic conductivity of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ composite electrodes with inactive material content at different PVDF/AB ratios.

conductive when there is no AB addition due to the electric insulating property of PVDF binder. At a PVDF/AB ratio of 5:1, an increase in the electronic conductivity with increasing total inactive material content is observed from 3% to 10%, after which the conductivity appears to level off. This is due to the conductivity limitation of the PVDF/AB composite at 5:1 ratio, as shown in Figure 1A. A continuous increase in the electronic conductivity with the total inactive material content is observed for the electrode with other PVDF/AB ratios. Again, at the same PVDF content, the electrode laminate exhibits the highest electronic conductivity at a PVDF/AB ratio of 5:4 compared with the others. This is in agreement with the highest conductivity of PVDF/AB composite at 5:4 ratio, as seen in Figure 1A. The electronic conductivity starts to decline at a PVDF/AB ratio of 5:5, which is believed to arise from the poor connectivity between particles as a result of the shortage of binder.

Electronic conductivity of an electrode laminate is a factor of the electrode impedance during electrochemical cycles. In general, electrode impedance is the sum of ohmic resistance, Li charge transfer resistance at the electrode/electrolyte interface and Li diffusion resistance within the cathode. Although increasing inactive material content contributes to the electronic conductivity at most of the PVDF/AB ratios, the increase in electronic conductivity will not have much impact on the electrode impedance if the electronic conductivity is an order of magnitude or more higher than the ionic conductivity of the electrode and the electrolyte.² Typically, the ionic conductivity of an organic electrolyte, such as 1 mol/dm³ LiPF₆/EC + DEC (1:1) adopted in this study, is ~0.01 S/cm at room temperature. The electronic conductivity for most of the cathode laminates prepared in this study is higher than the ionic conductivity of the electrolyte. Ionic conductivity of an electrode is not only closely related to the nature of the active material but also strongly affected by the inactive materials dispersed in the electrode.

Free-standing porosity is another parameter evaluating the cooperation between the electrode components. Figure 4 shows the variations of free-standing porosity of the electrode with the total inactive material content at different PVDF/AB ratios. A maximum porosity value is obtained for each PVDF/

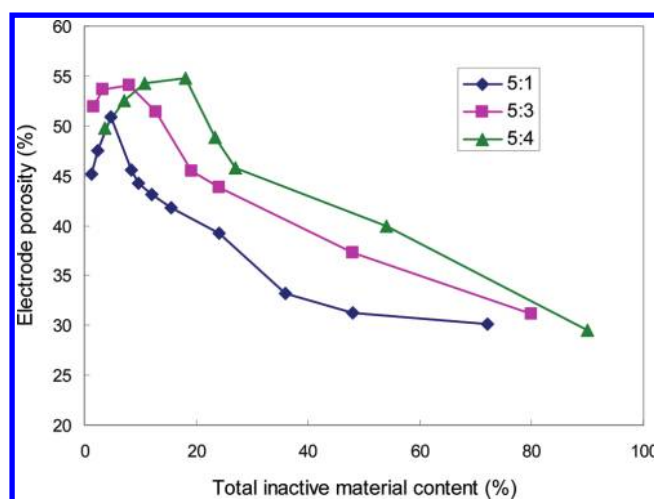


Figure 4. Variations of the free-standing porosity of the electrode with inactive material content at different PVDF/AB ratios.

AB ratio series with increasing inactive material content. Variation of the electrode porosity is associated with the percolation of the PVDF binder within the electrode. At extremely low inactive material content, the electrode laminate is shown to be a dense stack of the active material particles on the Al foil and, thus, has relatively low porosity. The dense stack of active material is spoiled by random distribution of a small amount of inactive materials. More voids or pores were generated within the electrode, leading to the increase in the electrode porosity. However, higher content of inactive material enables the formation of an interconnection network of PVDF chains in the electrode.^{13–15} On one hand, the percolation of PVDF makes closer contact between the particles. On the other hand, the open spaces between active particles are filled with the inactive materials, as shown in Figure 2. A decrease in the electrode porosity is thus observed. For the three series at different PVDF/AB ratios, the total inactive material content corresponding to its maximum porosity is different. The total inactive material content corresponding to its maximum porosity appeared at around 6% for the series at a 5:1 PVDF/AB ratio. By contrast, the total inactive material content of 18% was observed for the series at a 5:4 PVDF/AB ratio. This is because more PVDF is consumed in connecting the high surface area nanocarbon particles for the electrode containing inactive materials at a 5:4 PVDF/AB ratio, as compared with that at 5:1 PVDF/AB ratio. Although the free-standing porosity is affected by the cooperation between the electrode components, the electrode porosity is not considered as a factor influencing its electrochemical performances in this study because all the electrodes were calendered to 35% porosity prior to electrochemical test.

3.3. Electrochemical Properties of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Cathodes Containing Various Contents of Inactive Materials at Different PVDF/AB Ratios.

Figure 5 shows the charge–discharge profiles of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode containing 8% PVDF and different amounts of AB in the first electrochemical cycle. Clearly, the specific capacity of the cathode material is dependent on the electrode laminate formulation. At a C/10 rate, the first-charge capacities are about 185–190 mA h/g, and the first-discharge capacity falls in the range of 160–175 mA h/g. The discharge capacity of 175 mA h/g for the electrode containing 6.4% AB is consistent with the suggested specific capacity of

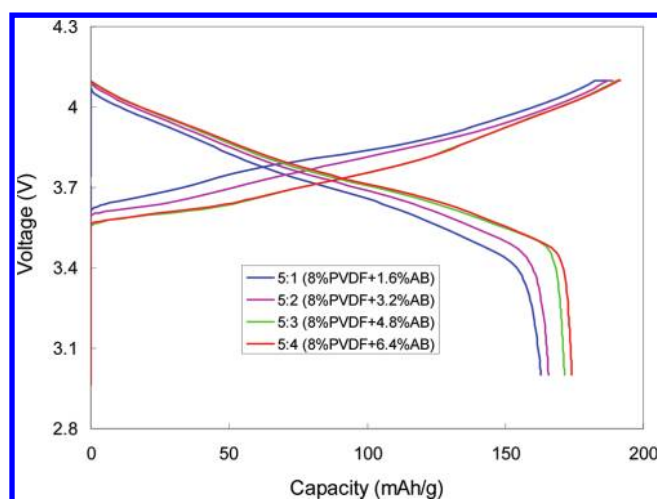


Figure 5. Charge–discharge profiles of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode containing 8% PVDF and different AB amounts at the first electrochemical cycle.

173 mA h/g when cycled between 3 and 4.1 V. The first Coulombic efficiencies (defined as the total discharge capacity divided by the total charge capacity in the first cycle) for the electrode containing 1.6%, 3.2%, 4.8%, and 6.4% AB content were 86.7%, 87.7%, 89.4%, and 90.8%, respectively.

The increase in the first Coulombic efficiency is resulted from a couple of sources. One is the electronic conductivity improvement of the laminate. At the same PVDF content, the laminate conductivity is increased from 0.27 S/cm at a 5:1 PVDF/AB ratio to 0.98 S/cm at a 5:4 PVDF/AB ratio. Another reason is ascribed to the increase in the ion conductivity of the electrode resulting from the less free PVDF binder in the electrode. PVDF is known to be ionic insulating, which hinders the migration of lithium at the electrode/electrolyte interface during electrochemical processes.¹⁶ At the same PVDF content, there are fewer free PVDF molecules in the electrode containing a high level of AB additive, since a large fraction of the PVDF is consumed in connection with the high surface nanocarbon particles. The increase in both electronic and ionic conductivity of the electrode contributes to a higher utility of the active materials, which is responsible for the specific capacity and the first Coulombic efficiency increase.

The first Coulombic efficiencies for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes containing different inactive material contents at different PVDF/AB ratios are displayed in Figure 6. It is interesting to see that the trend of the first Coulombic efficiency with total inactive material content clearly depends on the PVDF/AB ratio. At a 5:1 PVDF/AB ratio, a monotonic decrease in the first Coulombic efficiency with increasing total inactive material content was observed. Although the electronic conductivity of the electrode is increased from 0.02 to 0.27 S/cm by increasing the total inactive material content from 2.4% to 18%, as shown in Figure 3, the utility of the active material is decreased.

A similar trend is observed for the cathode containing different amounts of inactive materials at a 5:2 ratio. This result illustrates that the electronic conductivity is not the most important factor affecting the electrodes performance. At a PVDF/AB ratio of 5:1 and 5:2, the ion-blocking effect of PVDF is dominant. A high content of free PVDF induces a large decrease in the ionic conductivity of the electrode. The

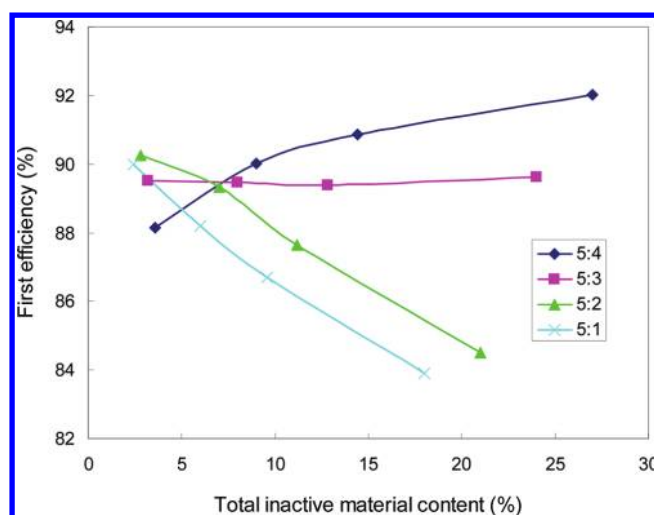


Figure 6. Variations of the first Coulombic efficiencies for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes with increasing inactive material contents at different PVDF/AB ratios.

decrease in the first Coulombic efficiency with increasing inactive material content is associated with a high ionic resistance and the resulting low active material utility of the electrode. At a PVDF/AB ratio of 5:3, the first Coulombic efficiency is seen almost independent of the total inactive material content. The inactive material composite is shown to be a trade-off between the electronic conductive effect of AB and the ion-blocking effect of PVDF. At a PVDF/AB ratio of 5:4, a slight increase in the first Coulombic efficiency is obtained with increasing inactive material content. It indicates that the conductive effect of AB has an advantage over the ion-blocking effect of PVDF at this PVDF/AB ratio. The relatively low Coulombic efficiency of the electrode containing 3.6% of inactive material at a PVDF/AB ratio of 5:4 results from the poor connectivity between particles due to the starve of binder.

Figure 7 shows the discharge curves of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode containing 8% PVDF and 4.8%

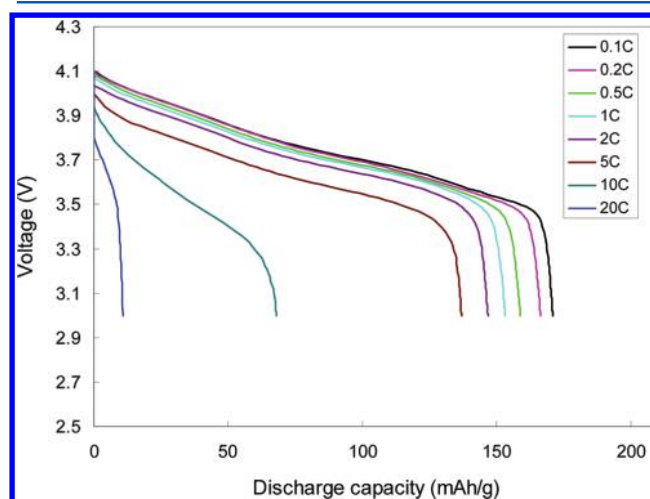


Figure 7. Discharge curves of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode containing 8% PVDF and 4.8% acetylene black at various C rates between 3.0 and 4.1 V.

acetylene black at various C rates between 3.0 and 4.1 V. The discharge capacity and discharge potential plateau is seen

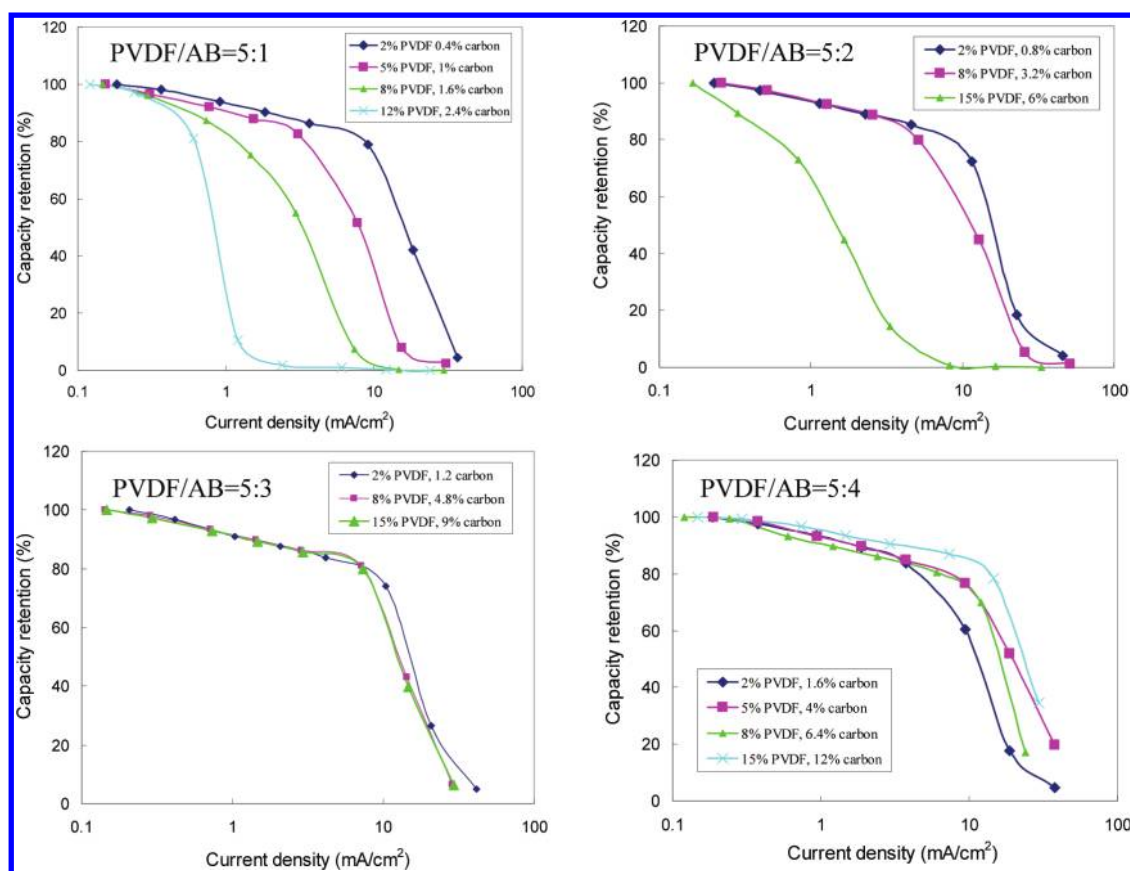


Figure 8. Capacity retention of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes containing different inactive material contents at different PVDF/AB ratios as a function of the C rate.

dropping with increasing discharge current density. The lowering of the discharge curve at a higher current is due to the polarization of the cell induced by the internal resistance of the cell. Capacity retentions of 86.0, 80.1, and 39.9% were obtained for the cathode at the 2 C, 5 C, and 10 C rates, respectively. It can be seen that 5 C is the maximum working current for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode. This result compares well with the literature values reported by Lu et al.,¹⁷ in which they got ~80% capacity retention at 2C with similar electrode loading of 10–11 mg/cm².

Figure 8 shows the capacity retention of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes containing different contents of inactive materials at different PVDF/AB ratios as a function of current density. Capacity retention is an evaluation of the ability of a battery at different rates to retain its capacity at very low current (0.1 C in this study) condition. At 5:1 and 5:2 PVDF/AB ratios, a good rate capability was obtained with a very low content of inactive materials. The electrode retains ~80% of its capacity at more than 10 mA/cm² current density. The rate performance is significantly deteriorated by increasing the total inactive material content, even with a large increase in the electronic conductivity of the laminates. It shows that the electrode impedance is not always in parallel with the electronic conductivity of the laminate. As we mentioned above, when the conductivity is higher than 0.01 S/cm, it will not be a deciding factor influencing the rate performance. Meanwhile, the increase in the total inactive material content at this PVDF/AB ratio induces a decrease in the ionic conductivity of the electrode as a result of the high content of free PVDF. The loss of rate capability at a higher inactive material content thus

results from the decrease in the ionic conductivity of the electrode.

At a PVDF/AB ratio of 5:3, the rate capability seems independent of the total inactive material content. It means that the ion-blocking behavior of the PVDF is offset by the appearance of more nanocarbon particles. A trade-off between the positive effect of the electronic conductivity of the AB and the negative effect of the ion-blocking behavior of the PVDF is obtained. This binder/carbon ratio is of scientific and technical importance for electrode optimization. At this ratio, the amount of inactive materials can be minimized to enhance the volumetric energy density of the electrode without loss of power density.

At a PVDF/AB ratio of 5:4, the rate capability is slightly enhanced by increasing the inactive material content. This is because the electronic conducting property is dominant for the inactive material composite. At a very low level of total inactive material content, the poor connection between the active and inactive particles due to the lack of PVDF binder is responsible for the loss of rate capability. A slight improvement in the rate performance can be achieved by using a very high content of inactive materials, for example, 15% PVDF and 12% AB; however, considering the density of AB and PVDF is considerably lower than that of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ active material, a large fraction of inactive materials implies a very thick electrode laminate at the same active material loading. The volumetric energy density of the electrode will be considerably decreased. In this sense, it is not a good strategy to use a very high level of inactive materials at this PVDF/AB ratio for a small enhancement of the rate performance.

By comparison between Figure 3 and Figure 8, the following conclusions can be derived: (1) the cooperation between active and inactive materials plays a subtle role in influencing the electrode performance; (2) optimizing the PVDF/AB ratio and content is important in fabricating a high-quality cathode electrode laminate; (3) the influence of the total amount of inactive material on the electrode performance is closely related to the PVDF/AB ratio. The competition between the electronic conducting effect of the AB and the ion-blocking effect of the PVDF explains the electrochemical behavior of the cathode as a function of the total inactive material content at different PVDF/AB ratios.

As shown in Figure 8, an elbow for each line appears at around 80% capacity retention. The current density corresponding to the 80% capacity retention was considered to be the maximum working current for the electrode. The higher the working current density, the lower the electrode impedance. To compare the rate performance of the cathodes of various compositions intuitively, the maximum current density for each electrode composition is plotted against its total inactive material content. The result is displayed in Figure 9. The same

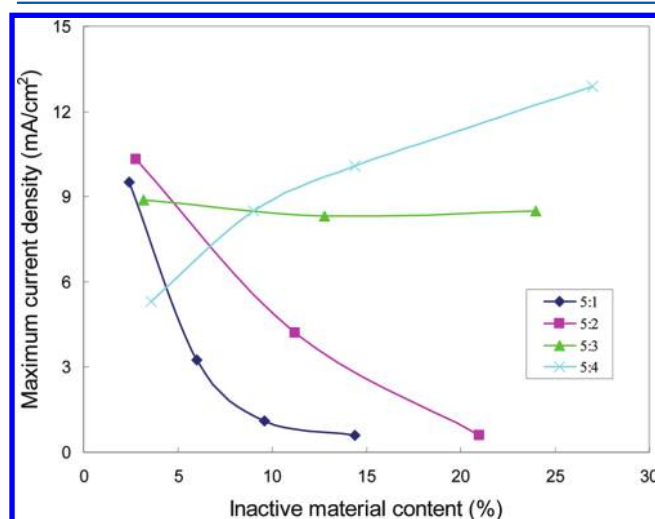


Figure 9. The maximum working current density for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes versus the total inactive material content at different PVDF/AB ratios.

variation trend is obtained for the rate capability with that of the first Coulombic efficiency (see Figure 6). The rate performance is deteriorated by the increase in the total inactive material content at 5:1 and 5:2 PVDF/AB ratios, whereas a slight increase is obtained with increasing total inactive material content at a 5:4 PVDF/AB ratio. It remains stable at different inactive material contents at 5:3 PVDF/AB ratio.

The same variation trend for the first Coulombic efficiency and the rate capability indicates that they are affected by the same origin. The origin is ascribed to the electrode impedance. Although there is a slight improvement of the rate performance with increasing inactive material content at a PVDF/AB ratio of 5:4, good results can be obtained only with a very high inactive material content. The use of a large amount of inactive materials leads to a decrease in the volumetric energy density of the electrode due to the low volume fraction of the active material, which is not desirable for PHEV applications.¹⁸ To

meet this requirement of high energy at moderate power levels, a 5:3 PVDF/AB ratio is recommended because one can improve the energy density of the electrode by reducing the total amount of inactive materials without a loss of its power density.

In addition to power and energy requirements, cycle life is another important criterion for lithium ion batteries for electric vehicles. To observe the effect of inactive material content on the long-term cycling performance of the cathode, the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode containing different amounts of inactive materials at a 5:3 PVDF/AB ratio was cycled against the MCMB anode as shown in Figure 10. The cathode

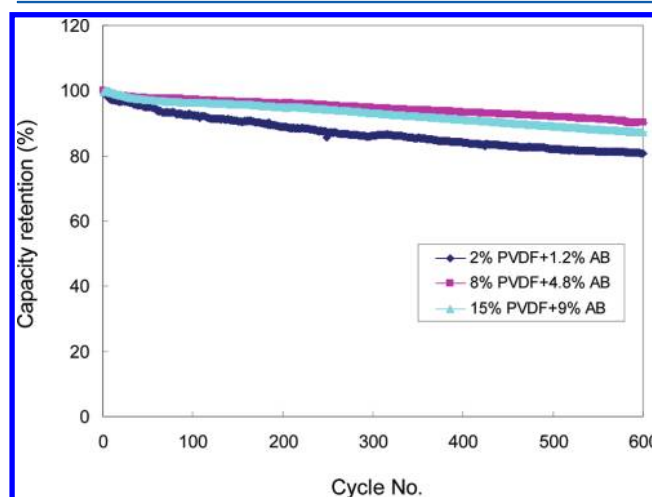


Figure 10. Cycling behavior of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode containing different amounts of inactive materials at a 5:3 PVDF/AB ratio against MCMB anode.

containing 2% PVDF + 1.2% AB shows relatively poor cycling behavior. This is believed to be associated with the poor mechanical properties of the electrode laminate. The electrode containing an extremely low level of inactive materials has a mechanical issue, since the percolation of PVDF binder is not developed as was discussed in Figure 4. Repeated expansion and contraction of the active material particles during Li insertion and removal can cause the particle isolation and thus leads to losing the active materials.^{19–21} With increasing total inactive material content at this PVDF/AB ratio, a mechanical issue will not be a problem as the percolation of PVDF is formed. An improved long-term cycling performance for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes containing 8% PVDF + 4.8% AB and 15% PVDF + 9% AB inactive materials was obtained. After 600 cycles, a capacity retention of more than 90% is obtained. This result is very good compared with those reported in the literature for the same cathode against a graphite anode.^{22,23} It should also be noted that the slightly better cycling performance of the cathode containing 8% PVDF and 3.2% AB compared with that containing 15% PVDF and 9% AB is believed to be associated with the experimental variation.

4. CONCLUSIONS

The cooperation among active material, PVDF binder, and conductive carbon plays a subtle role influencing the electrode's physicochemical properties and electrochemical performances. Although it is generally accepted that increasing conductive carbon contributes to high electronic conductivity of the

laminate, starving the binder also brings about a decrease in the electronic conductivity and electrochemical properties of the electrode because of a poor physical connection between the electrode particles. However, free PVDF in the electrode leads to a decrease in the ionic conductivity of the electrode due to the ion-blocking property of the ionic insulating binder.

The influence of the electrode composition on the electrode performance is related to the PVDF/AB ratio. At 5:1 and 5:2 PVDF/AB ratios, the first coulombic efficiency and rate performance of the electrode decrease with an increase in the inactive material content. At a PVDF/AB ratio of 5:4, increasing the inactive material content contributes to an enhanced first Coulombic efficiency and rate capability. The PVDF/AB ratio of 5:3 is the optimized recipe for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode. At this ratio, the first Coulombic efficiency and rate performance are stabilized, regardless of the inactive material content. The result is explained by the competition between the ion-blocking effect of PVDF and the electronic conducting effect of the AB in the electrode. At a PVDF/AB ratio of 5:3, the volumetric energy density of the electrode can be improved by using less inactive materials without loss of power density. However, taking the long-term-cycling performance into consideration, too low a content of the inactive materials is not recommended because the electrode may have a mechanical integrity issue. Finally, it needs to be stressed that the optimized PVDF/AB ratio of 5:3 for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode is specific to the categories of active and inactive materials adopted in this study. Nevertheless, the trend must be universal for lithium ion cathode containing oxide active materials, PVDF binder, and acetylene black.

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Notes

The authors declare no competing financial interest.

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