

# Effect of cathode binder on electrochemical properties of lithium rechargeable polymer batteries

Nam-Soon Choi, Young-Gi Lee, Jung-Ki Park\*

*Department of Chemical and Biomolecular Engineering, Centre for Advanced Functional Polymers, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, South Korea*

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## Abstract

The effect of polymer binder in the  $\text{LiCoO}_2$  positive electrode (cathode) on the electrochemical properties of this electrode is investigated. The positive electrode for lithium rechargeable polymer batteries (LPBs) is made by casting a solution of active material ( $\text{LiCoO}_2$ ), conducting material (super-P), polymer binder, and solvent. The irreversible capacity of the unit cell (Ligel polymer electrolyte/ $\text{LiCoO}_2$ ) is almost independent of the binder content and binder species in the cathode. In terms of specific capacity and the capacity retention with cycling, the optimum content of the binder is 8 wt.% and the cyclability is enhanced with an electrode containing a binder with better compatibility with liquid electrolyte.

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## 1. Introduction

Lithium rechargeable polymer batteries (LPBs) with gel polymer electrolytes have been widely studied [1–3]. The batteries typically consists of a positive electrode (cathode), i.e.  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  or  $\text{LiMn}_2\text{O}_4$ , a polymer electrolyte, and a negative electrode (anode), i.e. lithium graphitized or disordered carbon. The lithium-transition metal oxide-based cathode usually contains an active material, an electronic conducting agent, and a polymer binder [4–9]. Polymer binders allow the electrode to adhere to a current-collector and they also make active materials cohere, which is crucial for the good performance of electrodes and the unit cells based on gel polymer electrolytes. Nevertheless, studies on the effect of binder on the performance of cells have rarely been reported. This is addressed by varying the content and species of the binder in the cathode of a cell which uses lithium metal as an anode and a P(VdF-co-HFP)/PMMA blend as the gel polymer electrolyte.

## 2. Experimental

### 2.1. Preparation of polymer electrolyte

P(VdF-co-HFP) (Kynar 2801: HFP content 12 wt.%, Atochem) and poly(methyl methacrylate) (PMMA,  $M_w = 120\,000$ , Aldrich) were dried under vacuum at  $80\text{ }^\circ\text{C}$  for 24 h prior to use. A mixture of ethylene carbonate (EC)/propylene carbonate (PC) (1/1, w/w) containing 1 M  $\text{LiPF}_6$  was provided by Merck and used as received. The gel polymer electrolyte based on the blend of P(VdF-co-HFP) and PMMA was prepared by conventional solution casting using the mixture of acetone and tetrahydrofuran as a common solvent.

### 2.2. Preparation of cathode

$\text{LiCoO}_2$  as a cathode active material and super-P as a conductive agent were mixed in a ball mill. The binder solution (a mixture of polymer binder and solvent) was then added to the solid mixture to form a cathode slurry. The slurry was further mixed for 2 days in a ball mill and was then cast on an aluminum foil by means of a doctor blade. The cast slurries were dried at  $100\text{ }^\circ\text{C}$  for 30 min to evaporate the solvent, and dried further under vacuum at  $130\text{ }^\circ\text{C}$  for 12 h to remove the residual solvent. The dried cathode was pressed through a double-roll press to a thickness of about  $90\text{ }\mu\text{m}$ . The loading of active material corresponded to

\* Corresponding author. Tel.: +82-42-869-3925; fax: +82-42-869-3910.  
E-mail address: pjk@sorak.kaist.ac.kr (J.-K. Park).

Table 1  
Composition of cathodes

Cathode	Value (wt.%)				
	LiCoO <sub>2</sub>	Super-P	PVdF	Binder P(VdF-co-HFP)	PMMA
B1	88	7	5	–	–
B2	85	7	8	–	–
B3	84	7	9	–	–
B4	78	7	15	–	–
B5	85	7	–	8	–
B6	85	7	–	6.4	1.6

a capacity about 3 m Ah cm<sup>-2</sup>. The composition of the cathode is summarized in Table 1. The electrical resistance of the prepared cathode was obtained by a four-point probe method.

### 2.3. Cycle test of unit cell

Lithium polymer unit cells were made by sandwiching the blended gel polymer electrolyte between the cathode (LiCoO<sub>2</sub>) and the metallic lithium anode. The impedance of the cell was measured using a Solatron 1255 FRA. Charge–discharge tests of the Lilgel polymer electrolyte/LiCoO<sub>2</sub> cell (cell size = 4 cm<sup>2</sup>) were conducted in the voltage range 3.3–4.2 V at C/4 rate with galvanostatically controlled equipment.

## 3. Results and discussion

### 3.1. Effect of PVdF binder content in cathode on electrochemical behavior

In order to investigate the effect of the content of PVdF binder in the cathode on the electronic conduction, the electrical resistance of the electrode was measured as a function of the binder content. The results are plotted in Fig. 1. It is found that the electrical conductivity of the cathode increases and reaches a maximum, and then sharply decreases with increase of the PVdF content. An increase in the PVdF content can enhance the physical adhesion of the cathode to the current-collector and, thereby, cause the electronic conduction to increase. When the PVdF content in the cathode is too high, however, the micro-domain of the conducting agent (super-P) is separated by a greater distance, which results in hindered electronic conduction. As a result, there is an optimum PVdF content in the cathode where maximum electrical conductivity is obtained.

The initial impedance spectra of the Lilgel polymer electrolyte/LiCoO<sub>2</sub> cell with different amounts of PVdF binder in the cathode are presented in Fig. 2. The prepared cathode was soaked in a mixed solution of EC/PC/1 M LiPF<sub>6</sub> before cell fabrication. The bulk resistance of the polymer

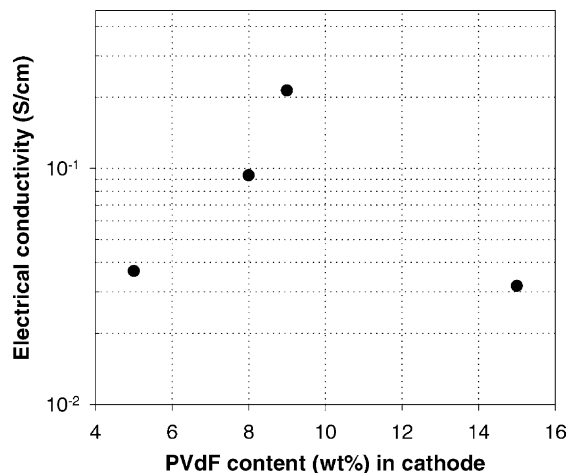


Fig. 1. Electrical conductivities of cathode with different PVdF contents.

electrolyte and its interfacial resistance with the lithium anode will be same for all cells tested since the cells are based on the same polymer electrolyte. Therefore, differences in the initial impedance among these cells are considered to originate from differences in the electrical conductivity and the ionic conductivity in the cathode. The decrease in the impedance of the unit cell with the amount of PVdF binder in the cathode is considered to be due to a reduction in the electrical resistance and an increase in the ionic conductivity of the electrode, as shown in Fig. 1 and Table 2, respectively. A high PVdF binder content can lead to an increase in the relative fraction of the amorphous region which absorbs liquid electrolyte into the cathode. When a high amount of liquid electrolyte is absorbed, the migration of solvated lithium ions in the cathode might become easier and faster by the formation of a sufficiently large region of the conducting phase of free ions inside the cathode. Thus, the ionic conductivity of the cathode increases with increase in PVdF content.

In spite of the high ionic conductivity of the cathode with a PVdF binder content of 15 wt.% the initial impedance of the unit cell is higher than that of the other cells with lower PVdF contents, as shown in Fig. 2. This is because an excess

Table 2  
Absorption of liquid electrolyte into cathodes and ionic conductivity of cathodes

Cathode	Absorption of EC/PC/1 M LiPF <sub>6</sub> (wt.% based on the binder)	Ionic conductivity (S cm <sup>-1</sup> ) (×10 <sup>3</sup> )
B1	43	1.4
B2	54	2.0
B3	60	2.8
B4	70	3.9
B5	67	3.5
B6	75	4.6

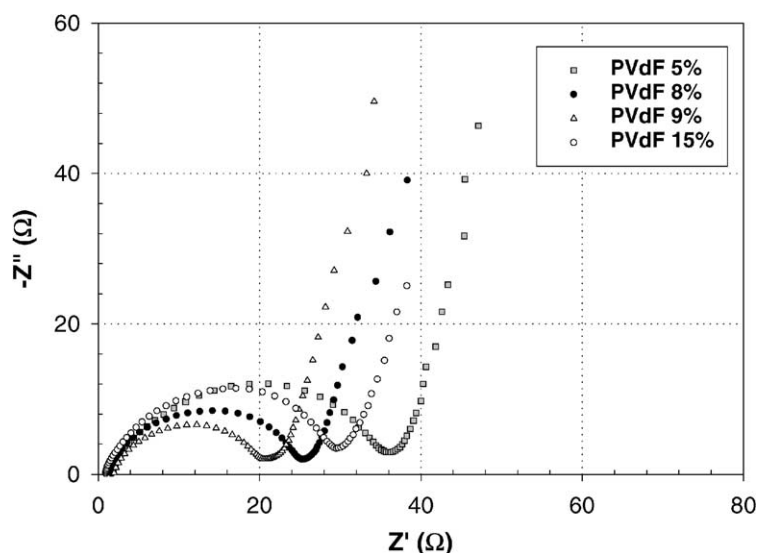


Fig. 2. Impedance spectra of unit cell (Lilgel polymer electrolyte/LiCoO<sub>2</sub>) before cycling as function of PVdF content in cathode.

of PVdF hinders electrical conduction through the conducting agent and the current-collector.

Charge–discharge curves for Lilgel polymer electrolyte/LiCoO<sub>2</sub> cells with different PVdF binder contents in the cathode are shown in Fig. 3. The curves were obtained at the *C*/10 rate in the voltage range 3.3–4.2 V for the solid electrolyte interphase (SEI) formation cycle. Increase in the PVdF binder content lowers the fraction of LiCoO<sub>2</sub> active materials at a given content of super-P conducting agent, as shown in Table 1. The charge and discharge capacities of the unit cell are thus found to decrease with increase in the PVdF binder content in the cathode. Since the irreversible capacity is dependent on the interfacial properties between the lithium anode and the polymer electrolyte, the irreversible capacities of the cells on the SEI formation

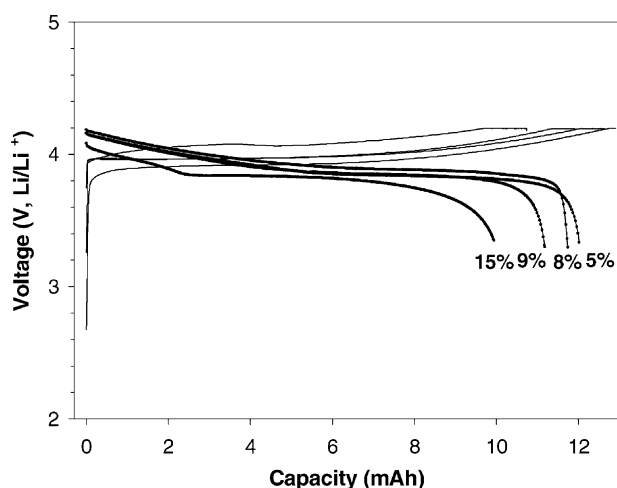


Fig. 3. Charge–discharge curves for unit cell (Lilgel polymer electrolyte/LiCoO<sub>2</sub>) as a function of PVdF content in cathode on first cycle (*C*/10 rate: 0.3 mA cm<sup>-2</sup>; voltage range: 3.3–4.2 V).

Table 3  
Irreversible capacity of Lilgel polymer electrolyte/LiCoO<sub>2</sub> cells

Unit cell	Cathode	Irreversible capacity (%)
C1	B1	7.0
C2	B2	7.1
C3	B3	6.9
C4	B4	7.4
C5	B5	7.0
C6	B6	6.9

cycle are nearly unchanged with change in PVdF binder content, as shown in Table 3.

The discharge capacities of Lilgel polymer electrolyte/LiCoO<sub>2</sub> cells with different PVdF binder contents in the cathode during the first five cycles are shown in Fig. 4. The cycle test was conducted at the *C*/4 rate in the voltage range 3.3–4.2 V. An increase in PVdF binder content results in a reduction in the discharge capacity of the unit cell, but can improve discharge capacity retention. Increase in the PVdF binder content can lead to fast migration of the free lithium ions in the cathode, as well as good interfacial contact with the blended gel polymer electrolyte due to a higher absorbance of liquid electrolyte, as shown in Table 2. In addition, it is expected from the impedance spectra in Fig. 2 that, with increase in binder content, the contact surface-area between the LiCoO<sub>2</sub> particles and the solvated lithium ion phase is increased, and thus, the intercalation–de-intercalation reaction of lithium ions on LiCoO<sub>2</sub> active material can easily occur. The use of excess PVdF binder results in an IR drop in the unit cell due to hindrance of electronic conduction in the cathode and thus, the discharge capacity retention becomes poorer, as shown in Fig. 4.

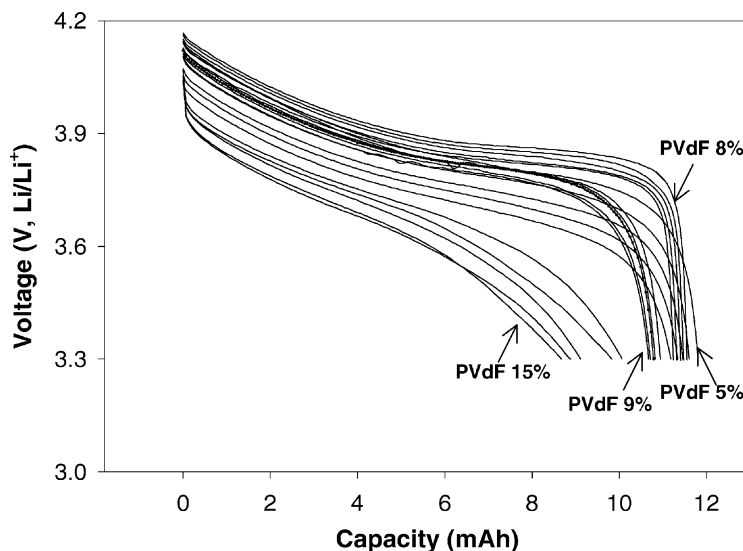


Fig. 4. Discharge curves of unit cell (Lilgel polymer electrolyte/LiCoO<sub>2</sub>) as a function of PVdF content in cathode during five cycles ( $C/4$  rate;  $0.75 \text{ mA cm}^{-2}$ ; voltage range: 3.3–4.2 V).

The specific capacity and the discharge capacity (%) of the Lilgel polymer electrolyte/LiCoO<sub>2</sub> cell on the fifth cycle as a function of the PVdF binder content in the cathode are presented in Fig. 5. It is found that the optimum PVdF binder content in the cathode is 8 wt.% in terms of both discharge capacity and capacity retention.

### 3.2. Effect of binder species in cathode on electrochemical behavior

In order to investigate the effect of binder species in the cathode on the electrochemical behavior of the unit cell,

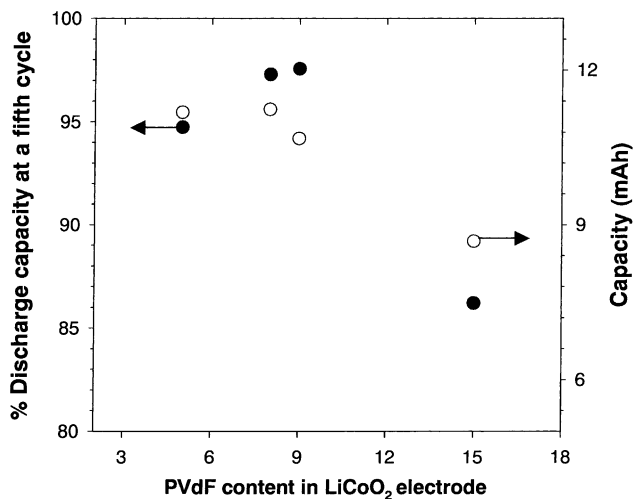


Fig. 5. Discharge capacity (%) and specific capacity of unit cell (Lilgel polymer electrolyte/LiCoO<sub>2</sub>) with different PVdF contents in cathode on fifth cycle.

the performance of P(VdF-co-HFP) and a blend of P(VdF-co-HFP) and PMMA (8/2, w/w) was compared.

The initial impedance spectra for a Lilgel polymer electrolyte/LiCoO<sub>2</sub> cell with different binders in the cathode before cycling are given in Fig. 6. When the gel polymer electrolyte based on a blend of P(VdF-co-HFP) and PMMA is used as a binder, the initial impedance of the cell is lower than that of a cell with a P(VdF-co-HFP) electrolyte. The amorphous phase fraction in the cathode will increase by introducing amorphous PMMA into P(VdF-co-HFP), and thus, there will be a higher absorption of liquid electrolyte and a faster migration of lithium ions in the cathode. When the gel polymer electrolyte based on the blend of P(VdF-co-HFP)/PMMA is used as a binder, the surface contact area between the cathode and the polymer electrolyte can also increase. The charge–discharge behavior of the unit cell (Lilgel polymer electrolyte/LiCoO<sub>2</sub>) during the SEI formation cycle and during the first five cycles ( $C/4$  rate) is shown in Fig. 7(a) and (b), respectively. The irreversible capacity loss during the SEI formation cycle is generally known to originate from decomposition of the organic solvent and lithium salt at the Lilgel polymer electrolyte interface [10,11]. In fact, the irreversible capacity loss of the unit cells is not dependent on the binder species in the cathode, as shown in Table 3.

The discharge capacity and the discharge capacity (%) of the unit cell with a containing a blend of P(VdF-co-HFP)/PMMA as a binder is higher than that of a cell with a cathode containing P(VdF-co-HFP), as shown in Figs. 7(b) and 8. This is mainly due to a large absorption of liquid electrolyte into the cathode. It can be seen that the amount of liquid electrolyte absorbed by a binder in the cathode can significantly influence the performance of lithium rechargeable polymer batteries.

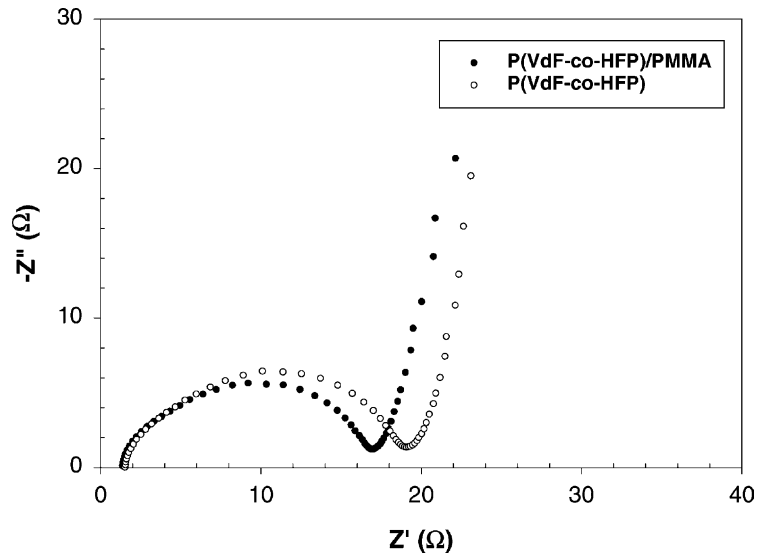


Fig. 6. Impedance spectra for unit cell (Lilgel polymer electrolyte/LiCoO<sub>2</sub>) containing P(VdF-co-HFP) and P(VdF-co-HFP)/PMMA blend as binders before cycling.

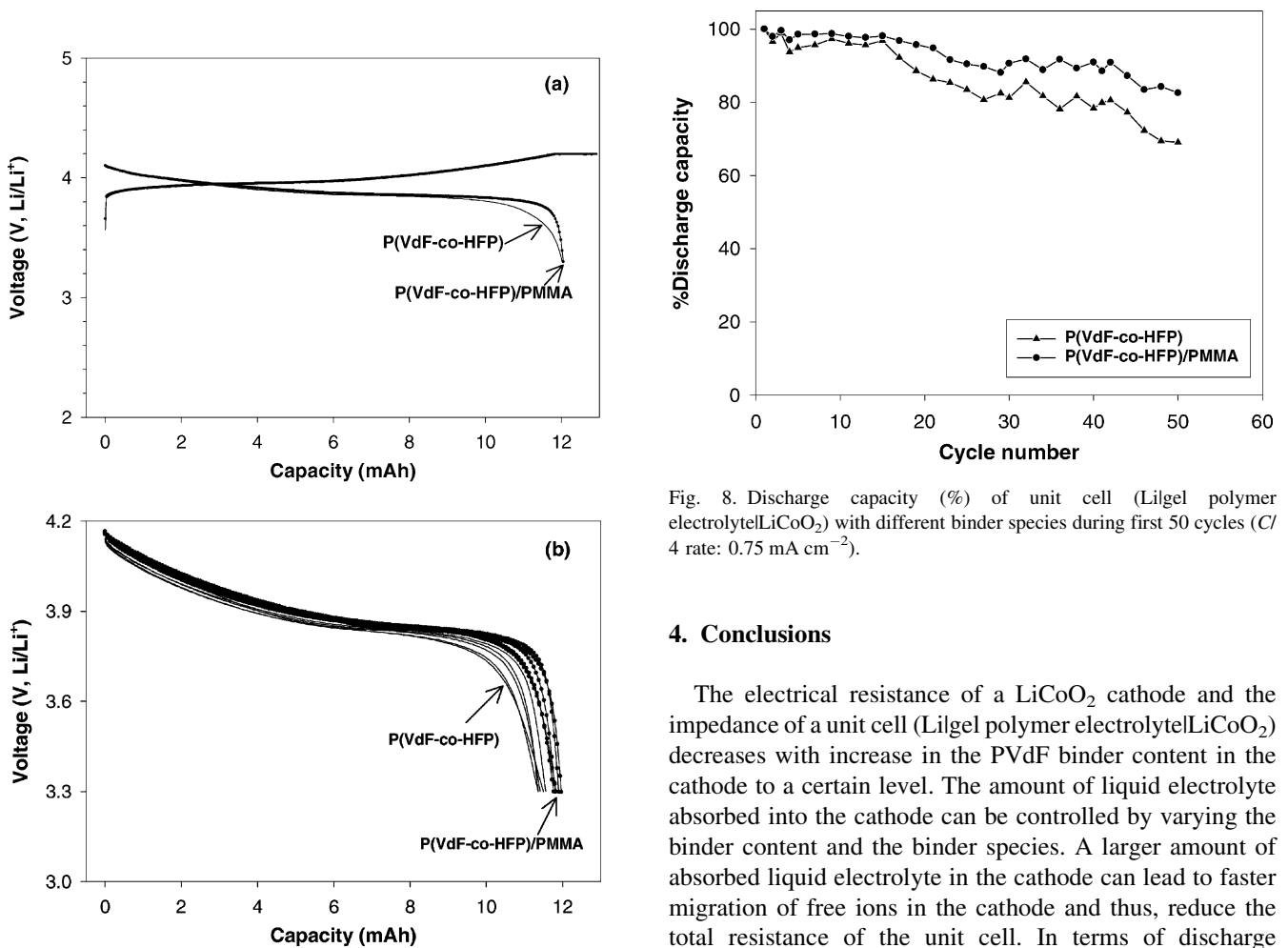


Fig. 7. Galvanostatic curves of unit cell (Lilgel polymer electrolyte/LiCoO<sub>2</sub>): (a) at SEI formation cycle (C/10 rate: 0.3 mA cm<sup>-2</sup>); (b) during first five cycles (C/4 rate: 0.7 mA cm<sup>-2</sup>).

#### 4. Conclusions

The electrical resistance of a LiCoO<sub>2</sub> cathode and the impedance of a unit cell (Lilgel polymer electrolyte/LiCoO<sub>2</sub>) decreases with increase in the PVdF binder content in the cathode to a certain level. The amount of liquid electrolyte absorbed into the cathode can be controlled by varying the binder content and the binder species. A larger amount of absorbed liquid electrolyte in the cathode can lead to faster migration of free ions in the cathode and thus, reduce the total resistance of the unit cell. In terms of discharge capacity and discharge capacity retention, there is found to be an optimum content (8 wt.%) of PVdF binder in the cathode for the performance of the unit cell. The binder

species should also significantly influence the electrochemical performance of the unit cell since the absorbed amount of the liquid electrolyte into the cathode depends on the nature of the binder.

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