Verification of Non-PFAS Materials as Cathode Binder for Lithium-ion Battery

Contents

Executive summary

This executive summary encapsulates the culmination of a rigorous analysis conducted to ascertain the most suitable binder material for cathodes in lithium-ion batteries (LiBs). The evaluation encompasses a diverse array of criteria, and the findings unequivocally establish Polyvinylidene fluoride (PVdF) as the optimal choice, surpassing alternative non-perfluorinated materials in fulfilling critical binder specifications.

This study effort involved a systematic comparison of various binder materials against a comprehensive set of criteria, as detailed in Table 9. These criteria encompassed coatability, electrolyte resistance, adhesion, long-term reliability, electrode processability, and potential stability. Through meticulous evaluation, PVdF emerged as a standout candidate, uniquely meeting all the specified requirements with exceptional performance.

The critical attribute of coatability, essential for ensuring uniform and efficient electrode fabrication, was found to be well-addressed by PVdF. Its ability to facilitate smooth and consistent coatings supports enhanced battery manufacturing processes. Furthermore, PVdF exhibited robust electrolyte resistance, a crucial factor for preventing binder degradation and maintaining stable battery operation over extended cycles.

Adhesion, a pivotal characteristic for promoting strong interfacial bonding within the electrode structure, was found to be notably superior in PVdF. This feature not only enhances electrode integrity but also contributes to overall battery performance and lifespan. The study also highlighted PVdF's long-term reliability, showcasing its capacity to withstand the rigors of extended usage without compromising its functional properties.

The processability of electrodes, a key determinant of manufacturability and performance, was demonstrated to be exceptionally favorable in PVdF-based systems. This material's compatibility with electrode processing techniques contributes to the seamless integration of PVdF into LiB production pipelines. Additionally, the potential stability exhibited by PVdF underscores its viability for sustained battery operation under varying conditions.

In contrast to the comprehensive suitability of PVdF, alternatives of non-perfluorinated binder materials were found lacking in fulfilling the entirety of the specified criteria. Consequently, this study unequivocally establishes PVdF as the optimal binder material for cathodes in LiBs, setting a new standard for binder performance and facilitating the advancement of high-performance and reliable energy storage technologies.

This study also highlights PTFE as the sole material endowed with the essential attributes to serve as a binder in the innovative dry process for electrode manufacturing. Its exceptional electrolyte resistance, electric potential stability, and sustained reliability over extended durations position PTFE as a promising choice. By adopting PTFE as a binder material, the LiB industry can potentially enhance electrode manufacturing processes, battery performance, and

overall longevity, thereby contributing to the advancement of energy storage technologies.

Introduction

Lithium-ion batteries largely consist of cathode (positive electrode), anode (negative electrode), electrolyte, and separator. A cathode is mainly made of active material, conductive agent, binder, and current collecting foil (aluminum foil). The binder plays the role of binding active materials and conductive agents together to fix on the current collector foil. In order to maintain battery performance and longer product life, it is known that excellent adhesion, electrolyte resistance and high potential stability are required for binders. PVdF (polyvinylidene fluoride) is widely known to be mainly used as the binder material. This study aims to verify the suitability of non-PFAS materials by comparing with PVdF and other materials.

1 List of Materials

The materials used in this study are shown in Table 1.

Table: 1 List of materials used in this study

	Binder Candidate Materials	Sample name	Molecular weight (×10,000)	1% Decomposition Temp. (°C)	Melting point (°C)
PFAS	Polyvinylidene di fluoride	**PVdF**	100	368.9	171.2
Non-PFAS	Linear Low Density Polyethylene	**LLDPE**	20	279.4	118.8
	Low Density Polyethylene	**LDPE**	27	272.9	109.3
	High Density Polyethylene	**HDPE**	180	287.1	131.3
	polystyrene	**PS**	16	267	-
	styrene-butadiene rubber (Styrene:Butadien =30:70 wt%)	**SBR**	14	330	Tg=93.8
	Hydrogenated nitrile-butadiene rubber (Acrylonitrile:Butadien =60:40 Hydrogenation rate=99%)	**H-NBR**	27	328.2	Tg=21.1
	Polyimide	**PI**	No data	521.4	385.5
	Polyamide	**PA**	1.9	330.6	180
	Polyethylene oxide	**PEO (Low-Mw)**	24	201.5	65
		PEO (High-Mw)	62	202.6	66.3
	Polyethylene glycol	**PEG (Low-Mw)**	1.9	214.6	64.1
		PEG (High-Mw)	53	210.3	66.7
	Polyvinyl alcohol	**PVA**	8.6	<100°C	-
	Polyacrylic acid	**PAA**	150	<100°C	-
	Polyvinylpyrrolidone (K-30)	**PVP**	2.0	<100°C	-
	Ethyl cellulose	**EC (Low-Mw)**	13	224.4	-
		EC (High-Mw)	18	230.6	-
	Methyl cellulose	**MC**	42	254.6	-
	Hydroxy propyl methyl cellulose	**HPMC**	18	243	-
	Carboxymethyl cellulose	**CMC**	463	<100°C	-

2 Validation methods

Figure 1 illustrates general manufacturing method for cathode binder for lithium-ion battery. Firstly, a cathode slurry is prepared by mixing active materials, conductive agent, binder and N-methyl -2 pyrrolidone (NMP) as a solvent. Next, the cathode slurry is coated on an aluminum current collector foil followed by drying process to obtain a cathode. Finally, in order to have stable electrode density, electrode processing completes by pressing process to manufacture the lithium-ion battery. The characteristics required for the lithium-ion battery binder include coatability (solubility to NMP, viscosity stability), electrolyte swelling (electrolyte resistance), long-term reliability (adhesion), and electric potential stability (voltage resistance). These verification methods are shown in Table 2.

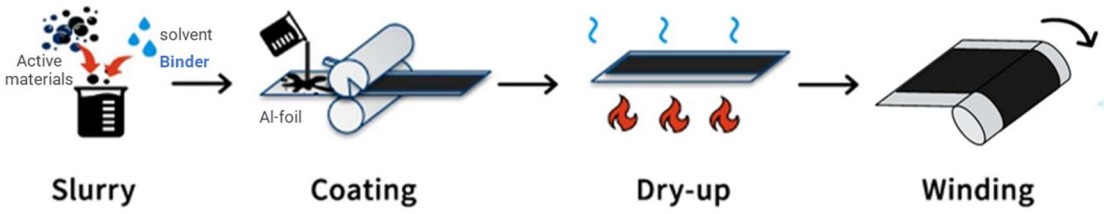

Figure 1: Example of cathode manufacturing process

Table 2: List of evaluation items

Evaluation items	Characteristics required	Verification method	Details
Coatability	solubility	Dissolution test	Evaluation based on dissolution in NMP
	coating viscosity stability	Viscosity measurement	Evaluation based on viscosity change rate immediately after slurry preparation
Electrolyte swelling property	electrolyte resistance	Electrolyte swelling test	Evaluation based on the ability to dissolve by immersion for a certain period and weight change
Long-term reliability	polar plate swelling	Peeling test	JIS K 6854-1 compliant 90 degree peeling test Evaluation by adhesion change before and after immersion in electrolyte
Potential stability	voltage resistance	LSV measurement	Evaluated by the voltage of the response current

3 Coatability

3.1 Solubility

As the cathode binder needs to be dissolved in NMP, solubility to NMP for various materials was evaluated. The cathode of the lithium-ion battery is obtained by mixing the cathode material with NMP to make the cathode slurry, then by coating it onto an aluminum foil followed by drying. A mixing rotor (VMRC-5, made by ASONE) with temperature controller function was used as an apparatus for dissolution. The dissolution was carried out at concentration of 5wt% with two different temperature, 25°C and 50°C. Dissolution was determined when the mixture becomes clear solution and there observed no residual solid content in the mixture.

Figure 2 and Table 3 show the evaluation results. The NMP-insoluble samples include six species: HDPE, LDPE, LLDPE, PI, PA, and CMC. These six materials were determined to be inappropriate as cathode binder as well as inapplicable.

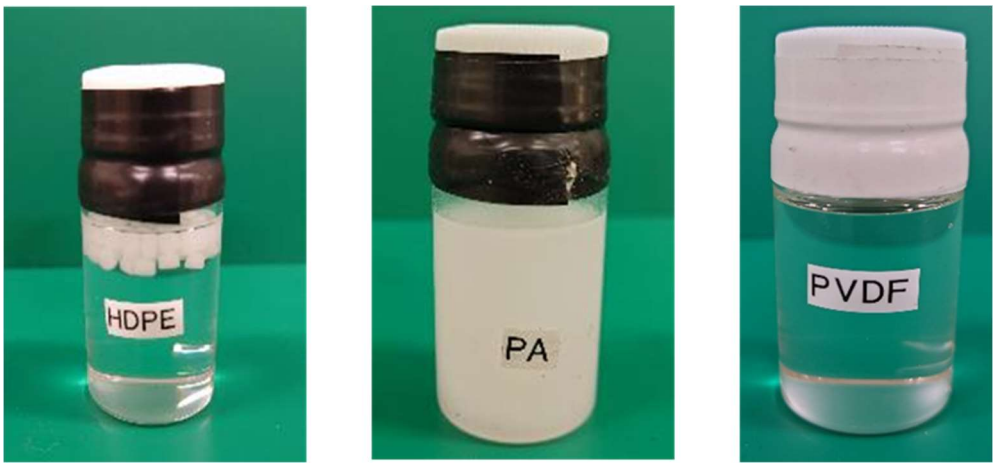

Figure 2: Picture of solubility test sample. HDPE (left, insoluble), PA (centre, insoluble), PVdF (right, soluble)

Table 3: List of test results (solubility)

Category	Sample name	25°C	60°C
PFAS	PVdF	Soluble	Soluble
Non-PFAS	LLDPE	Insoluble	Insoluble
	LDPE	Insoluble	Insoluble
	HDPE	Insoluble	Insoluble
	PS	Soluble	Soluble
	SBR	Soluble	Soluble
	H-NBR	Soluble	Soluble
	PI	Insoluble	Insoluble
	PA	Insoluble	Insoluble
	PEO (Low-Mw)	Insoluble	Soluble
	PEO (High-Mw)	Insoluble	Soluble
	PEG (Low-Mw)	Insoluble	Soluble
	PEG (High-Mw)	Insoluble	Soluble
	PVA	Soluble	Soluble
	PAA	Soluble	Soluble
	PVP	Soluble	Soluble
	EC (Low-Mw)	Insoluble	Soluble
	EC (High-Mw)	Insoluble	Soluble
	MC (High-Mw)	Insoluble	Soluble
	HPMC	Insoluble	Soluble
	CMC	Insoluble	Insoluble

3.2 Slurry preparation and viscosity stability

Next, feasibility of the cathode fabrication was evaluated. NMC811 (M2-C, BTR New Material Group Co., Ltd.) was used as an active material and carbon black (Super P Li, Imerys) as the conductive agent used for the cathode material. MAZERUSTAR (KK-1100 W, Kurabo Co., Ltd.) was used as a mixing device. The solid content of the binder slurry was fixed to 8wt% and all of them were prepared under the same condition.

The method for verifying paint stability is described in the following. In case of short pot life of the slurry, uniform coating cannot be achieved, hence the productivity decreases significantly. As an evaluation method, viscosity was measured using B-type viscometer (TVB-10M, Toki Sangyo Co., Ltd.) was conducted. The evaluation results are shown in Figure 3 and Table 4. When the observed viscosity change rate exceeds more than 300% after 1 day and 500% after 7 days from the initial viscosity value, it was determined to be “not applicable” to the cathode binder, as shown in red in Table 4. As for slurries for PVA, PAA, MC, and HPMC, since the fluidity have significantly decreased, coating procedure could not be performed. Thus, it was

determined that they cannot be applied to cathode binder for lithium-ion battery.

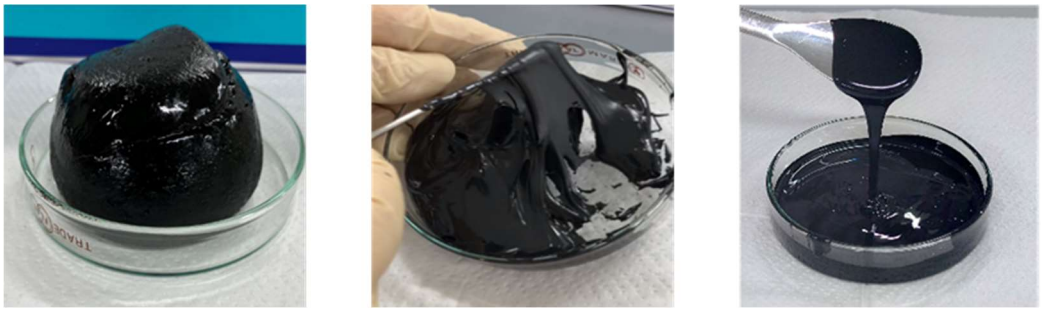

Figure 3: Pictures after coating test for PVA (left), PAA (centre), PVdF (right)

Table 4: Results for viscosity stability. Not applicable shown in red

Sample Name	Slurry Viscosity (%)	
	1day later	7days later
PVdF	88	333
PS	375	446
SBR	337	Not measurable (sedimentation)
H-NBR	145	215
PEO (low-Mw)	103	351
PEO (high-Mw)	100	81
PEG (low-Mw)	167	361
PEG (high-Mw)	91	273
PVA	>100,000 (range over)	>100,000 (range over)
PAA	>100,000 (range over)	>100,000 (range over)
PVP	250	>100,000 (range over)
EC	95	105
MC	>100,000 (range over)	>100,000 (range over)
HPMC	>100,000 (range over)	>100,000 (range over)

4 Electrolyte resistance and long-term reliability

4.1 Electrolyte resistance

The cathode binder for the lithium-ion battery generally requires moderate swelling with the electrolyte, as the lithium-ion conductivity is developed through the swollen electrolyte. However, when elution or dissolution to the electrolyte occurs, the durability of the cathode itself deteriorates, which leads to deterioration of the battery performance. Therefore, it is necessary for the cathode binder material not to dissolve in the electrolyte. Accordingly, electrolyte resistance was evaluated.

The verification method is as follows: (1) The sample (unprocessed, 15 mg) was immersed into an electrolyte (EC/EMC=3/7vol%). Dissolution was determined visually. (2) When casting of a film is possible to perform, by using the NMP solutions prepared in the section 3.1, a film (Thickness 200μm, Size Φ6mm) was made. Followed by immersing into the electrolyte solution for a certain period of time to observe the weight change (%) of the film. The temperature for storage was set at two levels (25°C and 60°C) for 7-days. The acceptable level of the weight change rate is determined to be within 150% after 7 days storage. The evaluation results are shown in Figure 4, Figure 5 and Table 5. The 6 samples, PVP, SBR, PEG, PEO, EC and H-NBR, were confirmed to be completely dissolved in the electrolyte. In addition, excessive swelling of HPMC was observed. It can be determined that the abovementioned samples are not applicable to the cathode binder for the lithium-ion battery, due to the poor electrolyte resistance.

Test method 1: Immersion and storage of sample (without processing) in electrolyte

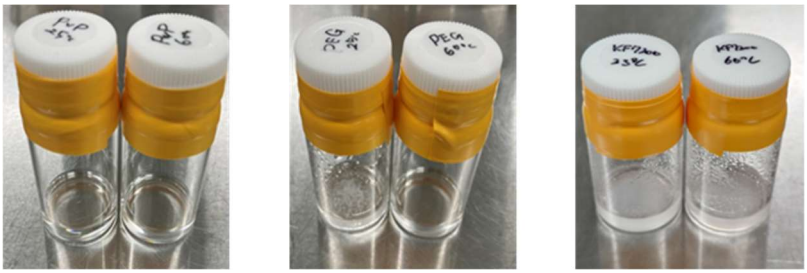

Figure 4 Pictures of electrolyte resistance test after 7days stored at 25°C (left), 60°C (right), PVP (left), PEG (centre), PVdF (right)

Test method 2: Immersion and storage of film samples in electrolyte

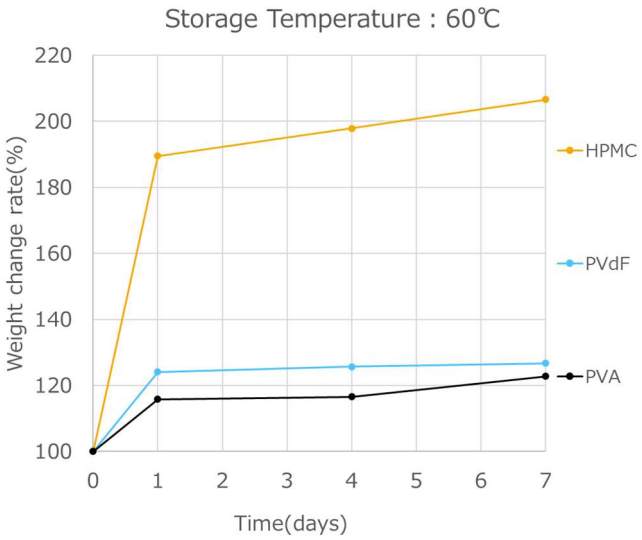

Figure 5: Test results (electrolyte resistance of the film)

Table 5: Electrolyte resistance test results

Category	Sample name	Test method 1 Electrolyte resistance		Test method 2 Weight change (%) at 60°C	
		25°C	60°C	1Day	7Days
PFAS	PVdF	Insoluble (Good)	Insoluble	124%	127%
Non-PFAS	PS	Insoluble	Insoluble	-	-
	SBR	Soluble (Bad)	Soluble (Bad)	-	-
	H-NBR	Soluble	Soluble	-	-
	PEO (Low-Mw)	Insoluble	Soluble	-	-
	PEO (High-Mw)	Insoluble	Soluble	-	-
	PEG (Low-Mw)	Insoluble	Soluble	-	-
	PEG (High-Mw)	Insoluble	Soluble	Soluble	Soluble
	PVA	Insoluble	Insoluble	116%	123%
	PAA	Insoluble	Insoluble	-	-
	PVP	Soluble	Soluble	-	-
	EC (Low-Mw)	Insoluble	Soluble	-	-
	EC (High-Mw)	Insoluble	Soluble	Soluble	Soluble
	MC	Insoluble	Insoluble	-	-
	HPMC	Insoluble	Insoluble	190%	206%

Weight measurements were conducted 1, 4, and 7 days after the start of immersion. On the

first day, PEG (Low-Mw, High-Mw), H-NBR, and EC dissolved to electrolyte hence determined to be unmeasurable. On the 7th day, it was confirmed that the weight change rate of HPMC exceeded 200% and the electrolyte resistance to be poor. In PVdF and PVA, on the other hand, it was confirmed that the weight change rate was about 120% and showed moderate swelling with the electrolyte. It was concluded that PVdF and PFA show excellent electrolyte resistance among other tested materials.

4.2 Polar plate swelling

Adhesion was evaluated as a long-term reliability. The main role of the cathode binder is to maintain and immobilise various material particles. Losing adhesion causes decrease in the entire battery life. As the evaluation method, a double-sided electrode (composition: NMC811/Super P Li/Binder=96/2/2(wt%) coating amount: 25 mg/cm^2) was firstly prepared by a press machine to set similar electrode density, followed by specimen preparation by cutting into a certain size. Next, to a PFA bottle electrolyte solution (EC/EMC=3/7vol%) was filled such that the specimen is fully immersed. It was then stored at 60°C. The long-term reliability can be evaluated by confirming the loss of the adhesion before and after immersion to the electrolyte. The results of the adhesion before and after immersion are shown in Figure 6 and Figure 7 and Table 6. With respect to PVP, PS, EC, PEG, and PEO, it could not be measured due to desorption and peeling of the electrode assembly after 1 day of immersion. It is understood that the swelling of the electrode plate was so high that desorption and peeling occurred, suggesting lack of long-term reliability. On the other hand, the observed electrode changes for PVdF and H-NBR before and after immersion were smaller than the other materials, indicated by relatively higher adhesion.

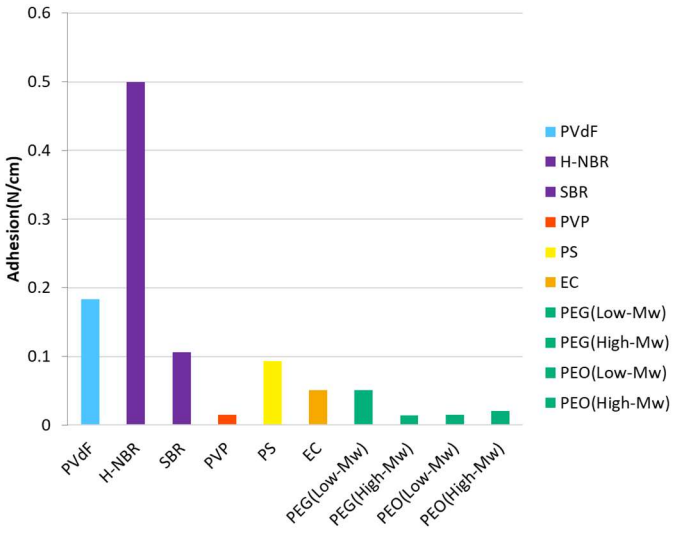

Figure 6: Adhesion test results (after coating)

Figure 7: Long-term reliability test: electrode observation after 1 day of immersion to electrolyte. PS (left), PVdF (right)

Table 6: List of study results (long-term reliability)

Sample name	After immersion in electrolyte Adhesion (%)	
	1day	7days
PVdF	88%	84%
H-NBR	88%	101%
SBR	78%	75%
PVP	0%	0%
PS	0%	0%
EC	0%	0%
PEG (Low-Mw)	0%	0%
PEG (High-Mw)	0%	0%
PEO (Low-Mw)	0%	0%
PEO (High-Mw)	0%	0%

5 Electric potential stability

5.1 LSV evaluation

The necessity for stability (oxidation resistance) of the cathode binder in a high potential state stems from the electromotive force generated by the potential difference between the battery's positive and negative electrodes. Inadequate oxidation resistance not only leads to cathode deterioration and gas generation, thereby degrading battery performance, but also poses risks such as ignition and battery rupture. To assess binder oxidation resistance, linear sweep voltammetry (LSV) measurements were conducted at 50°C, comparing response current magnitudes at 4.2 V and 4.45 V. A conductive aid, carbon black (Super P Li, from Imerys), was combined with the binder at a 1:1 mass ratio using NMP to create a paste; subsequently, the resulting electrode was coated onto aluminum foil, dried at 120°C, and employed as the working electrode, with Li metal foil serving as the counter electrode. Response currents surpassing 10×10 -6 A/cm² at 4.2 V or 15×10 -6 A/cm² at 4.45 V were deemed unacceptable, indicating battery performance and safety concerns. Notably, PVdF demonstrated exceptional stability

relative to other materials, while H-NBR, PVA, PVP, PS, EC, and HPMC exhibited considerable degradation and poor potential stability, as depicted in Figure 8 and Table 7.

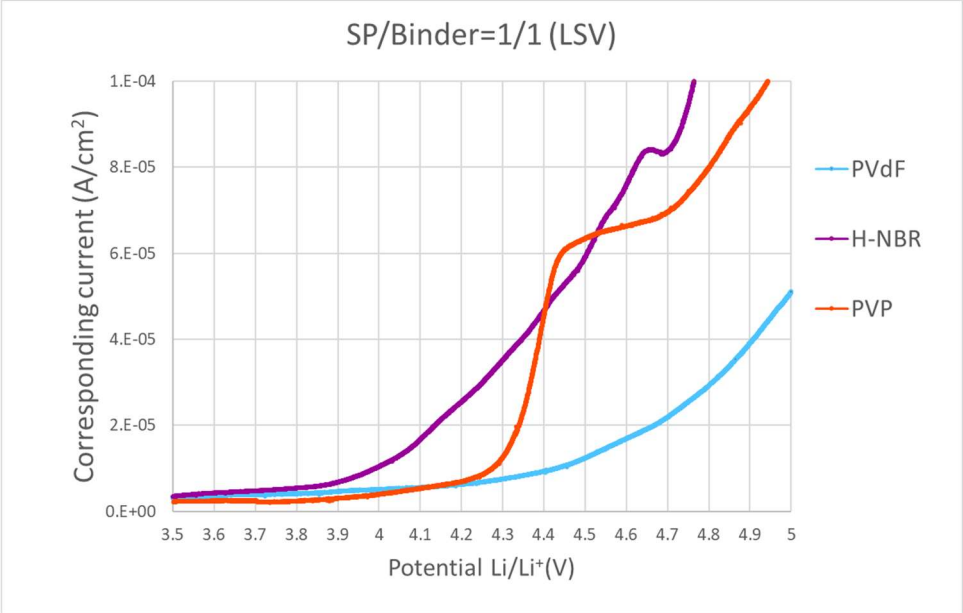

Figure 8: LSV measurement

Table 7: Electrical potential stability results

Sample	Corresponding current (A/cm^2)	
	4.2V	4.45V
PVdF	6.3×10^{-6}	10.4×10^{-6}
H-NBR	25.3×10^{-6}	52.7×10^{-6}
PVA	6.1×10^{-6}	15.7×10^{-6}
PAA	7.2×10^{-6}	13.4×10^{-6}
PVP	6.8×10^{-6}	61.5×10^{-6}
PS	9.0×10^{-6}	101.1×10^{-6}
EC	16.2×10^{-6}	39.9×10^{-6}
MC	7.0×10^{-6}	11.8×10^{-6}
HPMC	10.3×10^{-6}	19.3×10^{-6}

6 Conclusion

The analysis outcomes for diverse criteria are presented in Table 8, leading to the determination that PVdF uniquely fulfills the comprehensive set of requisite binder specifications encompassing coatability, electrolyte resistance, adhesion, long-term reliability, and potential stability, rendering other non-PFAS materials unsuitable for employment as cathode binders.

Table 8: Test result overview

	Sample NAME	Solubility in NMP		Slurry viscosity stability		Electrolyte resistance				After immersion in electrolyte Adhesion (%)		Potential stability	
				Viscosity change（%）				Test2 (Weight change(%), 60℃)				Corresponding current(A/cm2)	
		25℃	60℃	1day later	7 days latar	25℃	60℃	1Day	7 Days	1days	7days	4.2V	4.45V
PFAS	PVdF	Soluble	Soluble	88	333	Insoluble (Good)	Insoluble	124%	127%	88%	84%	6.3×10^{-6}	10.4×10^{-6}
Non-PFAS	LLDPE	Insoluble	Insoluble										
	LDPE	Insoluble	Insoluble										
	HDPE	Insoluble	Insoluble										
	PS	Soluble	Soluble	375	446	Insoluble	Insoluble			0%	0%	9.0×10^{-6}	101.1×10^{-6}
	SBR	Soluble	Soluble	337	Not measurable (sedimentation)	Soluble(Bad)	Soluble(Bad)			78%	75%		
	H-NBR	Soluble	Soluble	145	215	Soluble	Soluble			88%	101%	25.3×10^{-6}	52.7×10^{-6}
	PI	Insoluble	Insoluble										
	PA	Insoluble	Insoluble										
	PEO (Low-Mw)	Insoluble	Soluble	103	351	Soluble	Soluble			0%	0%		
	PEO (High-Mw)	Insoluble	Soluble	100	81	Insoluble	Soluble			0%	0%		
	PEG (Low-Mw)	Insoluble	Soluble	167	361	Insoluble	Soluble			0%	0%		
	PEG (High-Mw)	Insoluble	Soluble	91	273	Insoluble	Soluble	Soluble	Soluble	0%	0%		
	PVA	Soluble	Soluble	>100,000 (range over)	>100,000 (range over)	Insoluble	Insoluble	116%	123%			6.1×10^{-6}	15.7×10^{-6}
	PAA	Soluble	Soluble	>100,000 (range over)	>100,000 (range over)	Insoluble	Insoluble					7.2×10^{-6}	13.4×10^{-6}
	PVP	Soluble	Soluble	250	>100,000 (range over)	Soluble	Soluble			0%	0%	6.8×10^{-6}	61.5×10^{-6}
	EC (Low-Mw)	Insoluble	Soluble			Insoluble	Soluble						
	EC (High-Mw)	Insoluble	Soluble	95	105	Insoluble	Soluble	Soluble	Soluble	0%	0%	16.2×10^{-6}	39.9×10^{-6}
	MC	Insoluble	Soluble	>100,000 (range over)	>100,000 (range over)	Insoluble	Insoluble					7.0×10^{-6}	11.8×10^{-6}
	HPMC	Insoluble	Soluble	>100,000 (range over)	>100,000 (range over)	Insoluble	Insoluble	190%	206%			10.3×10^{-6}	19.3×10^{-6}
	CMC	Insoluble	Insoluble										

7 Experimental section

7.1 Pretest preparation

7.1.1 Experimental material

7.1.1.1 Measurement of molecular weight (weight average molecular weight)

After being weighed, the sample was allowed to dissolve overnight at room temperature in a predetermined quantity of eluent, subsequently undergoing filtration through a 0.45 μm PTFE cartridge filter following gentle agitation; for instance, PVdF was subjected to gel permeation chromatography (GPC) analysis, wherein calculations were based on data derived from the flow of dimethylformamide (DMF) solvent at a flow rate of 1.0 ml/min using AS-8010, CO-8020, and a column setup (3 GMHHR-H connected in series) from Tosoh Corporation, in conjunction with RID-10 A equipment from Shimadzu Corporation (molecular weight calculated with reference to polystyrene). Specific variations in testing conditions for each sample are outlined in Table 9.

Table 9: List of GPC conditions

Category	Binder Candidate Materials	Sample name	Test method		
			Eluent *1	Converted molecular weight	Temperature (°C)
PFAS	Polyvinylidene di fluoride	**PVdF**	DMF	PS	40
Non-PFAS	Linear Low Density Polyethylene	**LLDPE**	TCB	PS	140
	Low Density Polyethylene	**LDPE**	TCB	PS	140
	High Density Polyethylene	**HDPE**	TCB	PS	140
	Polystyrene	**PS**	THF	PS	40
	Styrene-butadiene rubber	**SBR**	THF	PS	40
	Hydrogenated nitrile-butadiene rubber	**H-NBR**	THF	PS	40
	Polyimide	**PI**	Not measurable		
	Polyamide	**PA**	HFIP	PMMA	40
	Polyethylene oxide	**PEO (Low-Mw)**	Water (Sodium nitrate)	PEG/PEO	40
		PEO (High-Mw)	"Water (Sodium nitrate)"	PEG/PEO	40
	Polyethylene glycol	**PEG (Low-Mw)**	"Water (Sodium nitrate)"	PEG/PEO	40
		PEG (High-Mw)	"Water (Sodium nitrate)"	PEG/PEO	40
	Polyvinyl alcohol	**PVA**	"Water (Sodium nitrate)"	PEG/PEO	40
	Polyacrylic acid	**PAA**	"Water (Phosphate buffer solution)"	PEG/PEO	40
	Polyvinylpyrrolidone	**PVP**	"Water (Sodium nitrate)"	PEG/PEO	40
	Ethyl cellulose	**EC (Low-Mw)**	THF	PS	40
		EC (High-Mw)	THF	PS	40
	Methyl cellulose	**MC**	Sodium Nitrate solution,0.1M	Pullulan	40
	Hydroxy propyl methyl cellulose	**HPMC**	Sodium Nitrate solution,0.1M	Pullulan	40

	Carboxymethyl cellulose	**CMC**	Sodium Nitrate solution,0.1M	Pullulan	40

*1 DMF: N,N-dimethylformamide, TCB: Trichlorobenzene, THF: Tetrahydrofuran, HFIP: 1,1,1,3,3,3-Hexafluoro-2-propanol

7.1.1.2 Thermal gravimetry/differential thermal analysis (TG/DTA)

Differential thermal analysis (TG/DTA7200, Hitachi High-Tech Science Co., Ltd.) was employed to measure mass changes, employing a temperature rise rate of 10°C/min within a temperature range from room temperature to 600°C under an air atmosphere, thus determining the temperature at which a 1% mass decrease occurred.

7.1.1.3 Differential scanning calorimetry (DSC)

Utilising a differential scanning calorimetry (DSC822e, Mettler Toledo) instrument, temperature was incrementally increased from 30°C to 220°C at a rate of 10°C/min, followed by a decrease to 30°C at the same rate, and subsequent elevation to 220°C at 10°C/min, with the melting point identified as the temperature corresponding to the peak heat of fusion during the second temperature ramp to 220°C.

7.1.1.4 Binder solution preparation

The binder solution, consisting of the binder dissolved in NMP at a concentration of 8 mass%, was prepared utilising a temperature-controlled mixing rotor (VMRC-5, ASONE) as the dissolution apparatus.

7.1.2 Slurry preparation

The binder-prepared cathode active material, NMC811 (M2-C, BTR), and a conductive agent, Super P Li Carbon Black (Imerys), were combined and homogenised using a planetary centrifugal mixer (KK-1100 W, Kurabo Co., Ltd.) to formulate a slurry; if the resultant slurry's viscosity exceeded 10,000 mPa·s, appropriate adjustment was accomplished by introducing NMP and subsequent re-stirring, until a viscosity of 10,000 mPa·s or less was achieved.

7.1.3 Fabrication of electrodes

Electrodes were fabricated through the uniform application of the acquired slurry onto both surfaces of a cathode current collector, consisting of an aluminum foil with a 20 μm thickness, aiming for an application mass of 25 mg/cm²; subsequent to this, complete evaporation of NMP solvent occurred at 120°C, culminating in the production of a cathode with an electrode mixture density of 3.4 g/cc via the application of pressure utilising a roll press machine.

7.1.4 Electrolyte preparation

To obtain a nonaqueous electrolyte, a blend of ethylene carbonate and ethyl methyl carbonate was prepared at a volume ratio of 30 to 70, followed by introduction of LiPF6 to achieve a concentration of 1.0 mol/L.

7.2 Evaluation method

7.2.1 Coatability

7.2.1.1 Solubility test

The binder solution was formulated by dissolving the binder in NMP, yielding a binder concentration of 5 mass% within the NMP solution; this process employed a temperature-controlled mixing rotor (VMRC-5, ASONE) as the dissolution apparatus, with dissolution conducted at two distinct levels, namely 25°C and 50°C. The resulting outcomes were categorised as follows: "Insoluble," characterised by the presence of solid particulates and turbidity, and "Soluble," denoting the absence of solid particles and the presence of a transparent solution.

7.2.1.2 Coating viscosity stability

Using a B-type viscometer (TVB-10M B-10M, Toki Sangyo), the viscosity of the cathode mixture was measured 10 minutes after the commencement of measurement, with the following parameters: temperature at 25°C, rotor No. M4, and rotation speed of 6rpm. The viscosity change rate (Xn) was derived by comparing the viscosity of the cathode mixture (η0) immediately following its preparation with the viscosity (ηn) after one day, utilising the following equation

$$Xn=\eta n/\eta 0\times 100[\%]$$

Additionally, the viscosity change rate (Xm) was determined using the viscosity (ηm) recorded seven days after mixture preparation, calculated in the following equation.

$$Xm=\eta m/\eta 0\times 100[\%]$$

7.2.2 Electrolyte resistance and long-term reliability

7.2.2.1 Electrolyte immersion test

The experimental specimens were prepared by segmenting 15 mg of the untreated sample and placing it within a 20cc glass screw tube, followed by the addition of 1.5cc of an electrolyte blend consisting of ethylene carbonate and ethyl methyl carbonate in a volumetric ratio of 30 to 70. Subsequently, the prepared test samples were subjected to storage within a temperature-

controlled bath at either 25°C or 60°C over a span of 7 days under static conditions, with visual inspection conducted to assess dissolution.

7.2.2.2 Electrolyte immersion test for film

The binder solution prepared earlier was uniformly coated onto a glass plate, followed by complete volatilization of NMP at 120°C to create a 200 mm film; subsequently, a Φ6mm-sized sample was punched out from this film, its mass (G0) was measured, and an electrolyte composed of a blend of ethylene carbonate and ethyl methyl carbonate at a volumetric ratio of 30 to 70 was added to 1.5cc within a 20cc glass screw tube housing the test sample. The assembly was then subjected to static storage at constant temperatures of 25°C and 60°C for 7 days in a controlled temperature bath. After removal, the dipped sample's mass (Gn) was measured post-electrolyte-wipe, enabling the calculation of the weight change rate (Xn) using the equation provided.

Xn=Gn/G0×100〔%〕

7.2.2.3 Polar plate swelling

A test specimen measuring 25 mm in width and 150 mm in length was prepared through segmentation of the aforementioned cathode; subsequently, the test specimen was fully immersed in an electrolyte, comprising a blend of ethylene carbonate and ethyl methyl carbonate at a volume ratio of 30 to 70, within a PFA bottle. The divided test portions were stored in a temperature-regulated bath at 60°C for periods of 1 day and 7 days, and upon removal from the bath, each sample was cleansed with ethyl methyl carbonate to eliminate ethylene carbonate residues. After washing, the samples were vacuum-dried at 25°C to ensure complete removal of the electrolyte, rendering them suitable for testing. The resulting test samples were affixed to a mobile jig using double-sided tape, whereupon a portion of the electrode was partially detached while the remaining segment was secured with a chuck. Subsequent stress measurement (N/cm) was conducted by subjecting the tape to a 90° pull at a rate of 100 mm/min, employing an autograph equipped with a 5N load cell.

7.2.3 Potential stability

7.2.3.1 LSV evaluation

The binder solution was formulated by dissolving the binder in NMP to achieve a binder concentration of 8 mass%; subsequently, carbon black (Super P Li, Imerys) was proportionally combined with the binder to establish a 1:1 mass ratio, followed by stirring the mixture for 10 minutes at a rotation speed of 2,000rpm using Awatori Rentaro (ARE-310, Shinky). Through the addition of NMP and subsequent re-stirring under the same conditions to achieve desired

viscosity, carbon paste was produced, which was then uniformly coated on one side of a 20μm-thick aluminum foil to attain a loading of 10 mg/cm². The electrode was fabricated by complete volatilization of NMP within a drying furnace at 120°C. By sandwiching the electrode and a Li metal disk (Φ15 mm) with a microporous polyethylene film (separator) of 20 mm thickness, and subsequently introducing the electrolyte prepared in section 8.1.4, a non-aqueous electrolyte was effectively impregnated into the separator, resulting in the assembly of a half-cell. After a 10-hour storage in a temperature-controlled bath at 50°C, the half-cell was linked to a Solartron 1255B + SI 1287 and subjected to a voltage sweep to 5V using a Li reference electrode, with a sweep rate of 0.1 mV/sec, facilitating the measurement of the response current.

8 Innovative dry electrode manufacturing: Exploring PFAS material for binder properties and performance enhancement

Introduction

In the realm of electrode manufacturing, a novel “dry process” has attracted attention, distinguishing itself from the traditional solvent-based coating approach. As illustrated in Figure 9, this process involves creating an electrode sheet through the amalgamation of active material, conductive agent, and binder in powdered form. The utilization of PFAS material, specifically PTFE powder, enables the formation of a sheet by binding the active components and conductive agent through applied force, yielding PTFE fiber. Given the unique attributes exhibited solely by PTFE as a binder, the subsequent inquiry aims to authenticate its suitability for the intended purpose.

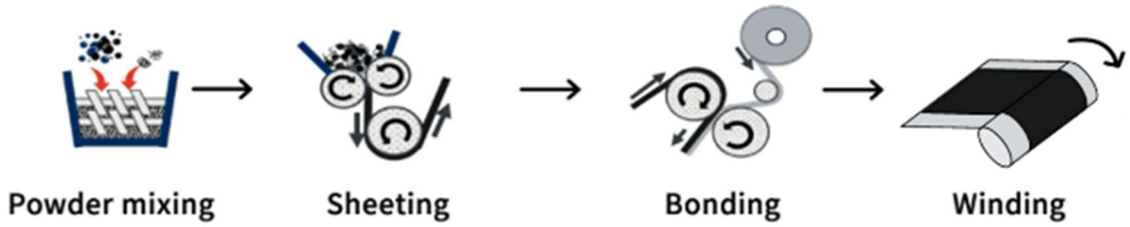

Figure 9: Electrode fabrication via Dry Process

8.1 Material used

POLYFLON PTFE F-104 (Daikin Industries, Ltd.) was used for this study. Table 10 shows basic characteristics of POLYFLON PTFE F-104.

Table 10: Basic characteristics of POLYFLON PTFE F-104

Items	Unit	Numeric value	Test method
Average Particle Size	μm	500	ASTM D 4895
Bulk Density	g/L	460	ASTM D 4895
Standard Specific Gravity	-	2.17	ASTM D 4895
Tensile Strength	MPa	45	ASTM D 4895
Elongation	%	400	ASTM D 4895

8.2 Validation method

8.2.1 Electrolyte resistance and long-term reliability

8.2.1.1 Electrolyte resistance

The degradation resulting from the elution and dissolution of the positive electrode binder within lithium-ion batteries undermines the inherent durability of the positive electrode, consequently contributing to a decline in battery performance. As such, ensuring resistance to dissolution within the electrolyte becomes an imperative criterion. To validate this attribute, we conducted an electrolyte resistance assessment. This involved immersing a 15 mg of POLYFLON PTFE F-104 sample into an electrolyte (EC/EMC = 3/7 vol%) and visually observing any signs of dissolution. The experiment encompassed two distinct environmental temperatures, namely 25°C and 60°C, and extended over a storage period of 7 days. The verification process conclusively affirms the electrolyte stability of PTFE, signifying its viability as a binder material.

Figure 10: Pictures of electrolyte resistance test for PTFE,
after 7days stored at 25°C (left), 60°C (right)

8.2.1.2 Polar plate swelling

Adhesion was evaluated as a long-term reliability. The main role of the cathode binder is to maintain and immobilise various material particles. Losing adhesion causes decrease in the entire battery life. As a method of assessment, the electrode sheet, prepared following the procedure detailed in Experimental Section 8.5, was precision-cut into a standardised test piece size (25 mm in width and 150 mm in length) before being meticulously positioned within a PFA bottle. It was made sure that electrolyte (EC/EMC=3/7vol%) was filled such that the test piece was fully immersed. It was then stored at 60°C. The long-term reliability can be evaluated by confirming the loss of the adhesion before and after immersion to the electrolyte. As a result, it demonstrated the absence of any discernible impact from immersion within the electrolytic solution. Moreover, the electrodes exhibited no instances of delamination, thus leading to the

determination of a commendably robust long-term reliability.

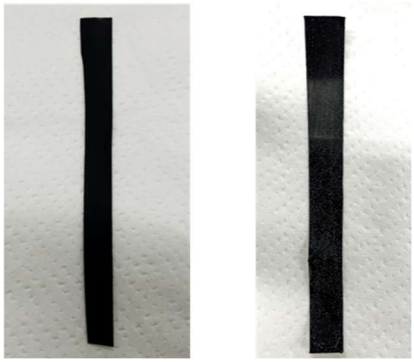

Figure 11: Long-term reliability test: electrode observation after 1 day of immersion to electrolyte, before immersion (left), after immersion (right)

8.3 Electric potential stability

8.3.1 LSV evaluation

The necessity for stability (oxidation resistance) of the cathode binder in a high potential state stems from the electromotive force generated by the potential difference between the battery's positive and negative electrodes. Inadequate oxidation resistance not only leads to cathode deterioration and gas generation, thereby degrading battery performance, but also poses risks such as ignition and battery rupture. To assess binder oxidation resistance, linear sweep voltammetry (LSV) measurements were conducted at 50°C, comparing response current magnitudes at 4.2 V and 4.45 V. A conductive aid, carbon black (Super P Li, from Imerys), was combined with the binder at a 1:1 mass ratio by preparing the mixture through a process of powder mixing and kneading, the resultant amalgam was meticulously affixed onto a carbon-coated aluminum foil utilising a precision pressing apparatus. This meticulously crafted electrode subsequently served its designated purpose as a functional working electrode, with Li metal foil serving as the counter electrode. This verification revealed that it exhibits oxidation resistance comparable to, if not exceeding, that of PVdF.

Table 11: Electrical potential stability results

Sample	Corresponding current (A/cm^2)	
	4.2V	4.45V
PVdF	6.3×10^{-6}	10.4×10^{-6}
PTFE	5.5×10^{-6}	10.1×10^{-6}

8.4 Conclusion

In light of discussion above, it is concluded that PTFE stands as the sole material endowed with the requisite attributes to serve as a binder in dry processes, owing to its exceptional electrolyte resistance, electric potential stability, and sustained reliability over extended durations.

8.5 Experimental section

8.5.1 Fabrication of electrode sheets

Electrodes were fabricated through the following steps: The positive electrode active material NMC811 (M2-C, BTR), PTFE, and carbon black (Super P Li, Imerys) were combined in a weight ratio of 96:1:1, milled in a tabletop mill (OML-2P, Osaka Chemical) and subsequently mixed at 10000 rpm for 1 minute to create a homogenised mixture. This mixture was kneaded for 5 minutes in a mortar and then processed in a desktop roll mill (Atlas150, MARCTO) to form a sheet. Placing this sheet onto an aluminum foil with conductive coating (Hosen), it was further processed using a roll press machine (0.5m/min, 60°C, 8KN) to produce an electrode with a current-collecting foil.

Additionally, for potential measurement, an electrode utilising carbon black (Super P Li, Imerys) as a conductive agent was prepared, with a carbon black to binder mass ratio of 1:1, using a similar process involving mixing, kneading, sheet formation, and roll press machine processing.

8.5.2 Electrolyte preparation

A non-aqueous electrolyte was obtained by blending ethylene carbonate and ethylmethyl carbonate in a volumetric ratio of 30:70, followed by the addition of $LiPF_6$ to achieve a concentration of 1.0 mol/L.

8.5.3 Electrolyte immersion test

The experimental specimens were prepared by segmenting 15 mg of the untreated sample and placing it within a 20cc glass screw tube, followed by the addition of 1.5cc of an electrolyte blend consisting of ethylene carbonate and ethyl methyl carbonate in a volumetric ratio of 30 to 70. Subsequently, the prepared test samples were subjected to storage within a temperature-controlled bath at either 25°C or 60°C over a span of 7 days under static conditions, with visual inspection conducted to assess dissolution.

8.5.4 Polar plate swelling

A test specimen measuring 25 mm in width and 150 mm in length was prepared by

segmenting the previously fabricated positive electrode. Subsequently, PFA bottles containing the subdivided test samples were filled with an electrolyte mixture composed of ethylene carbonate and ethyl methyl carbonate in a volumetric ratio of 30:70, ensuring complete submersion of the test pieces for storage periods of 1 day and 7 days. Samples extracted from each storage interval were subjected to ethyl methyl carbonate washing to eliminate ethylene carbonate residues. Following washing, the samples were subjected to vacuum-drying at 25°C for complete electrolyte removal, rendering them suitable for testing. After affixing the acquired test samples to a mobile jig using double-sided tape, a section of the electrode was detached while the remaining segment was clamped with a chuck, enabling stress measurement (N/cm) through an autograph, with a 5N load cell employed for this purpose.

8.5.5 LSV measurement

An electrode of Φ13 mm diameter and a Li metal disc of Φ15 mm diameter were arranged in opposition, separated by a 20 mm thick microporous polyethylene film (separator), culminating in the assembly of a half-cell wherein the separator was effectively impregnated with the non-aqueous electrolyte. Following a 10-hour storage of the assembled half-cell within a temperature-controlled chamber at 50°C, it was subsequently connected to a Solartron 1255B + SI 1287 system, and the response current was quantified through a voltage sweep up to 5V with Li as reference, employing a sweep rate of 0.1mV/sec under controlled 50°C conditions.