



Original scientific paper

Assessment of poly(vinylidene fluoride) copolymer blends as recent binders for lithium-ion batteries with LiMn_2O_4 cathode

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Abstract

The binder composition of battery electrodes can be linked to their performance in different ways due to the remarkable impact of binder on the external properties of the battery. Even being electrochemically passive, the binding material in lithium-ion polymer battery electrodes significantly improves the operation metrics, including the cycle balance, capacity, and efficiency rate. This study compares the performance of LiMn_2O_4 cathode material, taking into consideration poly(vinylidene fluoride) (PVDF) binder mixed with other blended copolymers, such as polypropylene carbonate-poly(trimethylene carbonate) (PPC-PTMC) and polyethylene-poly(ethylene oxide) (PE-PEO). As a mostly amorphous polymer, the PPC-PTMC copolymer is seen to have outstanding mechanical qualities that help to improve the adhesion and structural homogeneity of electrode material. Conversely, PE-PEO copolymer offers improved ionic conductivity within the electrode and binder when used as a polymeric surface-active agent for conductive additives. Compared to unblended PVDF binder, the improved structure homogeneity of the electrode results in remarkably better capacity, efficiency rate, and cycle performance. These results suggest that modifying the PVDF binder by copolymer combination is a workable way to enhance the homogeneity of electrode composites and interfaces.

Keywords

Li-ion cell; active materials; electrode microstructure; mechanical properties; battery C rating

Introduction

Conventional lithium-ion polymer cells have evolved into a traditional energy storage technology used in a variety of portable consumer electronics devices [1-3]. Because of the advantages of these batteries, such as their light weight, high working voltage, high specific energy, longer cycle life, minimal self-discharge, and portability, their utility extends to other domains. In typical Li-ion cells, graphite serves as the anode, while phosphate or transition metal oxide serves as the cathode

electrode [4]. Generally, the electrode is composed of conductive additive compounds, a binder, and an active substance. High-capacity batteries have a smaller percentage weight of inactive electrode components, such as conductive additives and binders [5]. The degradation of electrodes caused by the deactivation of active materials is the main factor influencing the lifespan of lithium-ion batteries and the corresponding capacity fade. Therefore, a binder is required to preserve the electrode materials' structural integrity and allow for the interaction of the active components, carbon black, and electrolyte. The capacity to absorb electrolyte and the dispersion of carbon black may influence battery performance. Due to remarkable cohesiveness qualities between the electrode films and current collectors, as well as superior electrochemical and thermal properties, poly(vinylidene difluoride) (PVDF) is the binder that is most commonly employed for both the positive and negative electrodes of lithium-ion cells [6-8]. As battery technology advanced, there was a growing need to fabricate stable, high-quality electrodes with minimal polymer binders and outstanding structural homogeneity. As a result, most of the past efforts on binders have focused on creating novel polymers.

The early attempts on electrode binders were aimed at improving the adhesive qualities. A lithium-substituted polyacrylic acid-based polymer, a dispersant, and a nonionic organic polymer with at least one nitrogen atom make up the binder that improves adhesion at the positive electrode. Another effective and reasonably priced method of enhancing the long-term electrochemical performance was reported for silicon nanoparticles (SiNPs) based electrodes as a thoughtful design of polymer binders [9,10]. Because of its weak van der Waals force with the SiNP surface, the conventional polymer binder PVDF performs poorly as a binder material for SiNP-based electrodes. Material scientists have found that the most important task when designing polymer binders is to enable a stable conductive network around the active material. Many efforts have been made in this direction because binders with a higher adhesion force to the SiNP surface, such as covalent bonds and supramolecular interactions, can produce SiNP-based electrodes with improved electrochemical performance. The hydroxyl groups on the surface of SiNPs can form hydrogen bonds, or partially covalent bonds in some cases, with polymers containing polar groups like polyacrylic acid (PAA) [11], carboxymethyl cellulose (CMC) [12], alginate (Alg) [13], polyimide [14], polyacrylonitrile [15], poly(vinyl alcohol) (PVA) [16], carboxymethyl chitosan [17], and guar gum (GG) [18]. In order to create pressure-sensitive adhesives (PSAs) for SiNP-based electrodes, Pan *et al.* [19] reported the copolymerizing of acrylic acid (AA) and 2-ethylhexyl acrylate (2-EHA). For effective binding performance, the authors looked at a compromise between the density of interaction groups and viscoelastic characteristics. The outcome demonstrated the superior electrochemical performance of SiNP-based electrodes using PSA with 20 mol.% of 2-EHA (Si-PSA 20 %), obtaining an 83 % capacity retention at the 100th cycle, as opposed to 54 % for Si-PAA following activation. Furthermore, Si-PSA 20 % exhibited better cycling performance at high active material mass loading and current density [19].

The second endeavor involves creating a water-based binder technology that is more environmentally friendly. The most often utilized water-based binder systems are styrene-butadiene rubber (SBR) or a hybrid system of SBR blends with carboxymethyl cellulose (CMC) [20] and acrylonitrile binders [21], particularly in the case of anode for lithium-ion batteries. The introduction of environmentally beneficial bio-based solutions, such as cellulose, natural poly lactides, alginates, lignin, *etc.*, is greatly facilitated by water-soluble binders. Because of their capacity to optimize electrode processing, low environmental impact, and a wide variety of functional properties, bio-based binders for lithium-ion batteries (LIBs) are currently the subject of intense

research and industrial attention [22]. A wide variety of bio-based binders are available, each with a distinct surface functionality and polar and functional surface groups, including hydroxyl and carboxylic acid groups. Van der Waals, hydrogen, and covalent bond interactions can, therefore, be added to produce a variety of binding processes and ensuing interfacial strength [23]. Conversely, a study on composite materials based on water-soluble binders for electrochemical capacitors was carried out by Khomenko *et al.* [24]. Electrochemical capacitors work on the basis of their ability to store and release electrical energy through internal electrolyte ion distribution inside a double electric layer. The rate of ion transfer across the "electrode-electrolyte" interface in traditional redox processes seen in batteries is significantly slower than the rate of ion redistribution in the double electric layer. New electrochemical systems, electrode materials, and electrolytes have been the main subjects of recent scientific studies in the field of electrochemical capacitors [24].

The creation of multipurpose binders falls into the third group of attempts. Due to their potential contribution to increasing device capacity, multifunctional binders have attracted a lot of interest lately [25]. To create high-performance lithium-ion batteries cheaply and sustainably, the problem of low conductivity and insufficient mechanical stability of the electrodes can be solved with an ecologically friendly, highly conductive, and mechanically robust binder system. Conductive polymer binders like polyaniline (PANI) [26,27], polypyrrole (PPY) [28], and poly(3,4-ethylenedioxythiophene) (PEDOT) [29] are the most well-known examples. In order to support higher loading of electrode materials and significantly enhance the electronic interaction between conductive agents and active materials, conductive polymer binders are advantageous for electrochemical performances, such as increased energy and power density. A multifunctional network binder (MNB) was used by Park *et al.* [30] to create a new binder system to jointly enhance the electrochemical stability and performance of silicon-based electrodes. According to the authors, the incorporation of MNB into the Li-PAA-based electrode system results in an abundance of functional bridges that form a robust binding matrix. Furthermore, MNB with strong dispersion stability enhances the ionic conductivity of Si-based electrodes [30].

Apart from the aforementioned strategies, polymer blending or mixing offers an appealing method of creating a high-performance binder by merging the benefits of various polymers or attaining synergistic outcomes. The creation and functionality of PEO-PVDF composite binders for lithium-ion batteries were documented by Liang *et al.* [31]. Using an X-ray diffractometer (XRD) and a scanning electron microscope (SEM), the phase and morphology were determined. Electrochemical performance tests were also conducted, showing that the battery-specific discharge capacity decreased from 113 to 88 mAh g⁻¹ after 150 cycles, while the Coulomb efficiency stayed at roughly 99 %. Besides, the CV curve nearly matched 100 times, indicating exceptional cycle performance [31]. In order to improve the stability of silicon anodes, Wang *et al.* [32] reported on a robust block copolymer, PVDF-b-Teflon (PTFE), that can agglomerate the crushed silicon. It is possible to create elastic PVDF-b-PTFE with significant breaking elongations (>250 %), high viscosity, strong ionic conductivity, and heat stability using the suspension copolymerization of vinylidene fluoride and tetrafluoroethylene. The authors demonstrated how 5 wt.% of the binder creates elastic cobweb structures in the electrode matrix that effectively combine conductive agents and silicon particles to provide electrodes with long-term cycling stability and high-rate performance. The results indicated a viable approach to create extremely pliable and resilient binders for electrodes that experience significant volume changes throughout the electrochemical reactions [32]. Many new binders have already been developed for specific targets in the pursuit of higher energy density, such as solid-state batteries (SSBs), alloy-type cathodes and anodes with large volume

effect, and high-voltage (4.5 V) cathodes, where these binders demonstrate their various functions [33]. They might affect the components of the solid electrolyte interface, guarantee the stability of the electrode and electrolyte interface, move ions and electrons within the electrodes, and give flexibility and adhesion to solid-state electrolyte (SSE) films. In investigating binder roles in lithium batteries, Zhang *et al.* [33] concluded that enhanced functional binders would be essential to the development of high-energy-density LIBs and SSBs in the future. Nowadays, poly(vinylidene fluoride) (PVDF) is the most extensively used binder, despite some disadvantages that make it far from the perfect material. The non-conducting property, delayed electrolyte dissolution, and poor adhesion to the current collector limit its applicability as a durable binder for lithium-ion batteries intended for extended cycle life. A group of scientists from the Japan Advanced Institute of Science and Technology (JAIST) was looking into a novel kind of binder that is derived from a bis-imino-acenaphthenequinone-paraphenylene (BP) copolymer in an effort to find an alternative [34]. Additional research [35] has demonstrated that polymer blending can produce a more homogeneous morphological structure, impacting all solid constituents' interactions and dispersion.

In this paper, we used this approach in investigation of LiMn_2O_4 cathode with two distinct blend binders based on PVDF that feature different copolymers, poly(ethylene oxide) (PEO) and poly(trimethylene carbonate) (PTMC), with the addition of either polypropylene or polypropylene carbonate to the former and later, respectively. The present research is focused on better understanding how these blends based on PVDF affect the microstructure, interface, and electrochemical performance of electrode composites serving as LiMn_2O_4 cathodes in a lithium-ion battery cell.

Experimental

In 4 wt.% N-methylpyrrolidone (NMP), poly(vinylidene fluoride) (PVDF) binder solution (Sigma Aldrich) was dissolved. Polypropylene carbonate-poly(trimethylene carbonate) (PPC-PTMC) supplied by Empower Materials and poly(ethylene oxide)-poly(propylene carbonate) (PEO-PPC) solutions produced by Sigma Aldrich with a solid content of 5 wt.% in NMP were prepared in a water bath at a temperature of 80 °C. PVDF was the predominant component, and solutions of PVDF/(PPC-PTMC) and PVDF/(PEO-PPC) blends were created with percentage weights of 15, 25, and 100. LiMn_2O_4 powder (MTI Corp.), carbon black (SuperC45, MTI Corp.) as a conductive agent, and a binder at a set ratio of 91:5:4 by weight were used to create cathode samples. The slurry was ground with a mortar and pestle for twenty minutes before being cast onto aluminum foil with a casting blade. After that, most of the solvent was removed from the slurries by drying them at 80 °C for four hours. They were placed in an 80 °C vacuum oven to eliminate the solvent entirely. The dried slurry loading was regulated at $20 \pm 1 \text{ mg cm}^{-2}$.

To assess the microstructures of the cathodes, scanning electron microscopy (Phenom ProX Model, Netherlands) was employed. The smoothly made electrode was punched using a Precision pouch punching mold (Benzo Technology, China) to 50 μm . After that, the cathodes were dried in a vacuum furnace (TOB-DZF-6020, China) for around 12 hours to eliminate any moisture and leftover solvents.

The tested battery cell comprised the graphitic anode (length and width, 150 and 100 mm) coated on a copper current collector with LiMn_2O_4 cathode (length and width, 165 and 130 mm) coated on aluminium current collector at an electrode distance of 40 mm. The cell consists of a separator and electrolyte made of lithium salt in an organic solvent. A commercial polypropylene/polyethylene/polypropylene (PP-PE-PP) film (Celgard Corp 2400) was employed as the separator, and 1 M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate and ethyl methyl carbonate (EC:EMC) was used as the liquid electrolyte. The C-rates, charge and discharge capabilities of constructed cells were

examined using a Cadex C7400 battery analyzer. At room temperature, the battery was tested for 60 cycles of charge and discharge at a current rate of 0.2 C. To find the cell impedance, electrochemical impedance spectroscopy (Digatron EIS Meter, China) technique was used. The impedance measurements were carried out between the two terminals of the cell at a frequency range of 6.5 kHz to 1 mHz with an amplitude of 10 mV as AC excitation signal at a voltage of 4.2 V.

Results and discussion

A field emission scanning electron microscope was used to examine the surface morphology of spinel LiMn_2O_4 electrode and the possible impact of two composite binders, PVDF/(PPC-PTMC) and PVDF/(PE-PEO), respectively. First, SEM was used to examine the morphology of electrode composites made from two PVDF-based blends, as presented in Figure 1. As seen in Figure 1A, the distribution of PVDF and carbon black in the conventional binder PVDF is irregular, and there are a lot of exposed active material particles (LiMn_2O_4). The high extent of exposed active material particles indicates little contact within the composite, suggesting that the PVDF binder was unable to distribute the carbon black evenly. As displayed in Figures 1B to 1D, the electrode morphology for the PPC-PTMC-modified samples is compatible with experimental outcomes. The binder and conductive additive dispersion and distribution uniformity on the active material particles are improved by the addition of PPC-PTMC. The amorphous form of PPC-PTMC, which is extremely flexible at high molecular weight, may be the cause of improvement. Similarly, for the blends of PVDF/(PE-PEO) depicted in Figure 1E to 1G, it was discovered that the amount of binder and active material particles increases with an increase in PE-PEO content. This demonstrates how adding PE-PEO can improve carbon black dispersion and improve electrode composite interactions. The sample containing 100 wt.% PE-PEO as the binder exhibits a thick layer of carbon black and binder on the surface of the active material, indicating that the copolymer PE-PEO exhibits considerably better interaction with the active material, which is the primary factor responsible for the improvement in microstructures. The ionic conductivity is enhanced by the inclusion of the copolymer PE-PEO, which joins the microstructure of the active materials.

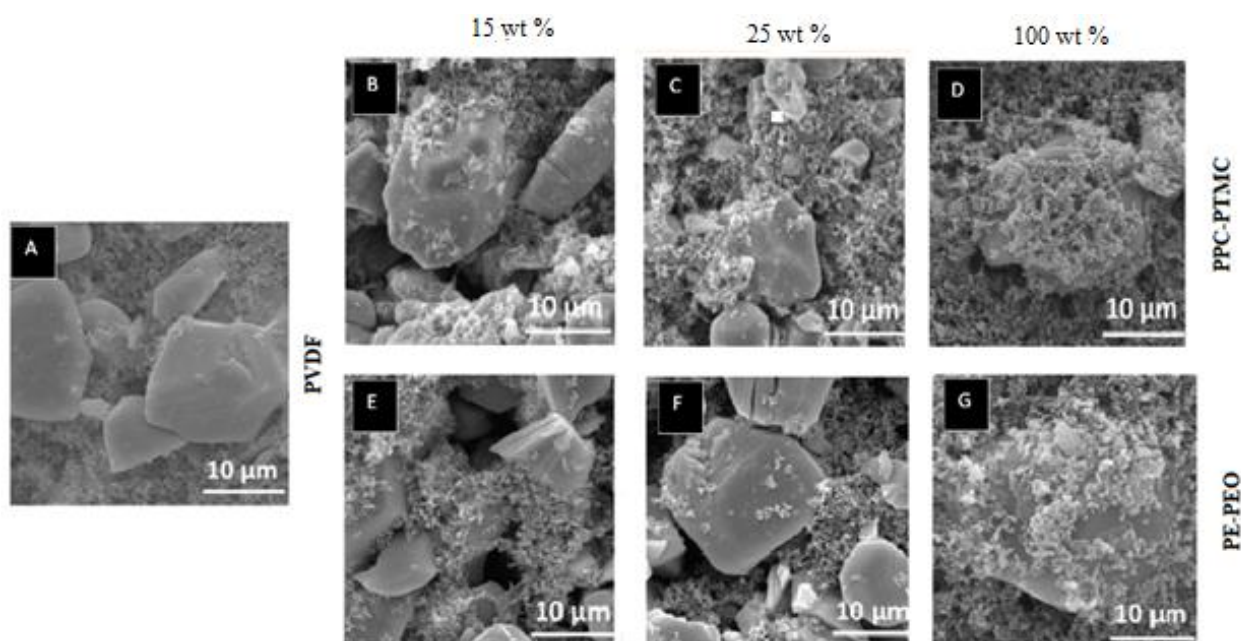


Figure 1. SEM images of electrodes prepared using PVDF blends with different amounts of PPC-PTMC and PE-PEO

The interactions between all components, the binder morphology, and the porous structure have significant roles in the mechanical properties of electrodes. An axial compression experiment involving an indentation test was used to characterize the mechanical properties of the active layer in compression. This method also measures compressive properties in the direction of electrode thickness. An axial compression experiment was conducted on damp electrodes submerged in liquid electrolytes for ten minutes in order to examine the impact of blend binders on the mechanical properties of electrodes. The outcomes of the axial compressing experiment are displayed in Figure 2. The linear region slope, and the electrode compression strength are connected. As Figure 2A illustrates, the mechanical characteristics of the PVDF binder decreases when PPC-PTMC is added, particularly at large loadings (e.g., 25 wt.%). However, the mechanical properties of the PVDF/(PE-PEO) blend binder remained good, as demonstrated in Figure 2(B), showing that the addition of PE-PEO to the PVDF did not adversely affect mechanical properties. To be more precise, the 25 wt.% PTMC electrode has a substantially smaller slope (0.5945) than PVDF electrode (0.8470). Furthermore, it was shown that the PPC-PTMC electrode control sample has the lowest mechanical characteristics, with the lowest slope of 0.3942. This is likely because PPC-PTMC swells well in liquid electrolytes (see Table 1 for the rate of electrolyte absorption). The rate of electrolyte absorption is the speed at which a measured electrolyte is absorbed within the battery. As shown in Figure 3, the rate of electrolyte absorption is measured as a slope from the graph of contact angle (θ) versus time.

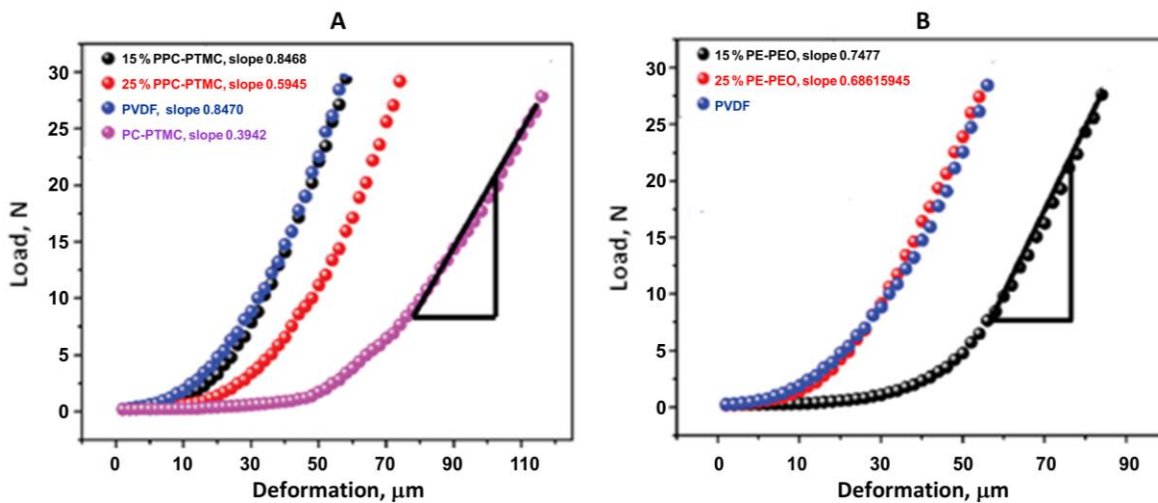


Figure 2. Impacts of binder combinations on the mechanical properties of damp electrodes

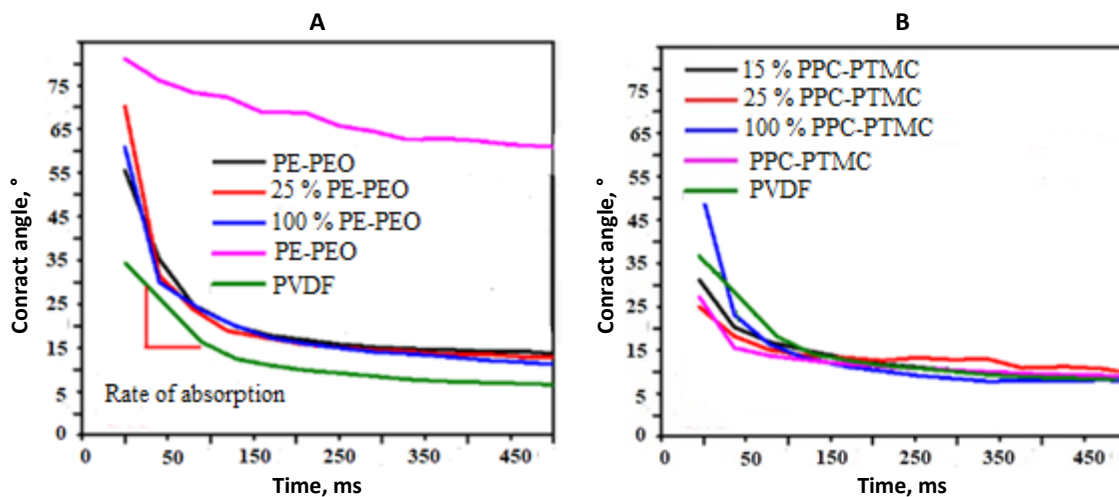


Figure 3. Wettability examinations with binders of PVDF blends for PVDF/PE-PEO and PVDF/PPC-PTMC electrode composite

Since the control electrode broke into tiny fragments after drying, the pure PE-PEO control sample was not compared. The addition of PPC-PTMC or PE-PEO to the PVDF binder can increase structural uniformity but not mechanical qualities, according to the results on microstructures and mechanical properties shown here.

Table 1. Rates of electrolyte absorption

Modifier loading, wt.%	Slope		
	PVDF/PPC-PTMC	PVDF/PE-PEO	Unblended PVDF
15	0.15	0.26	-
25	0.34	0.24	-
100	0.16	0.06	0.18

The morphological tests have shown that dispersion and distribution of carbon black and binder within electrode composites can be enhanced by combining PPC-PTMC and PE-PEO copolymers with PVDF binder.

The charge transfer resistance of the battery cells was studied using electrochemical impedance spectroscopy (EIS) in order to investigate further how the structural change affects the electrochemical performance. Nyquist plots of the battery cells containing different blended binder systems in comparison to the control samples are shown in Figure 4. Figure 4A shows that the impedance curves of PVDF and PPC-PTMC are fairly close, suggesting that their resistances are comparable. It appears that the SEM data, which demonstrated a notable improvement in carbon black uniformity, are at odds with this resistance result. However, because the liquid electrolyte can swell or even dissolve PPC-PTMC, the uniform conductive network might be compromised somehow. Consequently, the PPC-PTMC binder has dissolved or swelled inside the cell, negating the advantage in homogeneity. Figure 4(A) shows that in comparison to both PVDF and PPC-PTMC, the PVDF/(PPC-PTMC) mix may combine the benefits of both PPC-PTMC and PVDF, resulting in lower charge-transfer resistance, seen as the lower diameter of semicircle impedance response. It is noteworthy that internal battery resistance is the sum of electrolyte resistance between two electrodes, electrode materials resistance, separator resistance, current collector resistance and connection resistance. In Nyquist plots, internal battery resistance is determined by the intersection of the impedance curve with the real axis (Z') at the high frequency part of the spectrum. As shown in Figure 4(A), higher internal resistance is noticed for PVDF/(PPC-PTMC) 25 wt.%, because the uniform conductive network might be compromised by expanding PPC-PTMC, thereby increasing the internal battery resistance. This is most likely because the PPC-PTMC swells or dissolves in the binder. The mechanical characteristics of the electrode, which are based on PVDF/(PPC-PTMC) 25 wt.% as indicated in Figure 2(A), are further confirmed by this finding.

In the case of the PE-PEO modified binder system, charge transfer resistance from Figure 4(B) reduces as PE-PEO loading increases, in line with the morphological structures. The fact that PE-PEO can enhance the binder and carbon black network homogeneity, which is also stable with the liquid electrolyte, is most likely what led to this outcome. There are observable variations in the internal resistance of the samples based on Nyquist plots. Internal resistance is likely to be isolated from electrolytes and other resistances despite the difficulty of this. As shown in Figure 4, the lowest charge transfer resistance of 30.1Ω was recorded within the electrode by the PVDF/(PE-PEO) binder with 25 wt.% of PE-PEO, and 32.5Ω by the PVDF/(PPC-PTMC) binder with 15 wt.% of PPC-PTMC.

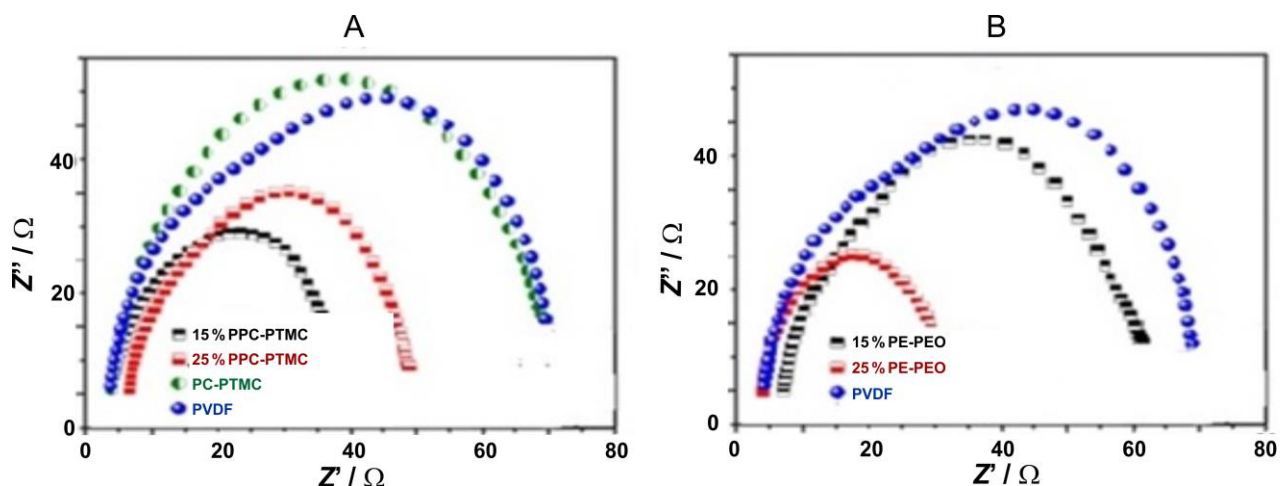


Figure 4. Nyquist plots for (A) PVDF/(PPC-PTMC), and (B) PVDF/(PE-PEO) blend binders

The assembled battery was tested for 60 charge and discharge cycles at the current rate of 0.2C at room temperature in order to confirm the cycle performance of the battery. Figure 5A illustrates that the PVDF/(PPC-PTMC) system with rational loading of PPC-PTMC can maintain the structure stability as did PVDF but improve the structure uniformity and, consequently, the specific capacity and C-rate capability. The PVDF/(PPC-PTMC) cells deliver higher specific capacity over all testing cycles. This outcome aligns with impedance research, as seen in Figure 4A. Higher specific capacity and internal resistance of the cell can be correlated by establishing linear fitting. PVDF/(PPC-PTMC) binder has cycling stability comparable to that of a pure PVDF binder. Semi-crystalline fluoropolymer PVDF has molecules with a big dipole moment perpendicular to the polymer chain, and it also has outstanding chemical stability, high mechanical strength, thermal stability, and aging resistance [36]. When PVDF and PVDF/PTMC are combined properly, usable materials with regulated strength, flexibility, and biodegradability are produced in agreement with structural characterization outcomes. According to Lee *et al.* [37], who reported on the synthesis and analysis of trimethylene carbonate copolymers microstructures using ¹³C NMR spectroscopy, the obtained results are consistent with the reaction mechanism and properties like crystallinity, strength, flexibility, solubility, and biodegradability. The PVDF and PVDF/PPC systems are seen to be able to retain their microstructures following cycling, even though PPC-PTMC inflated a little to produce a coating on the electrode surface.

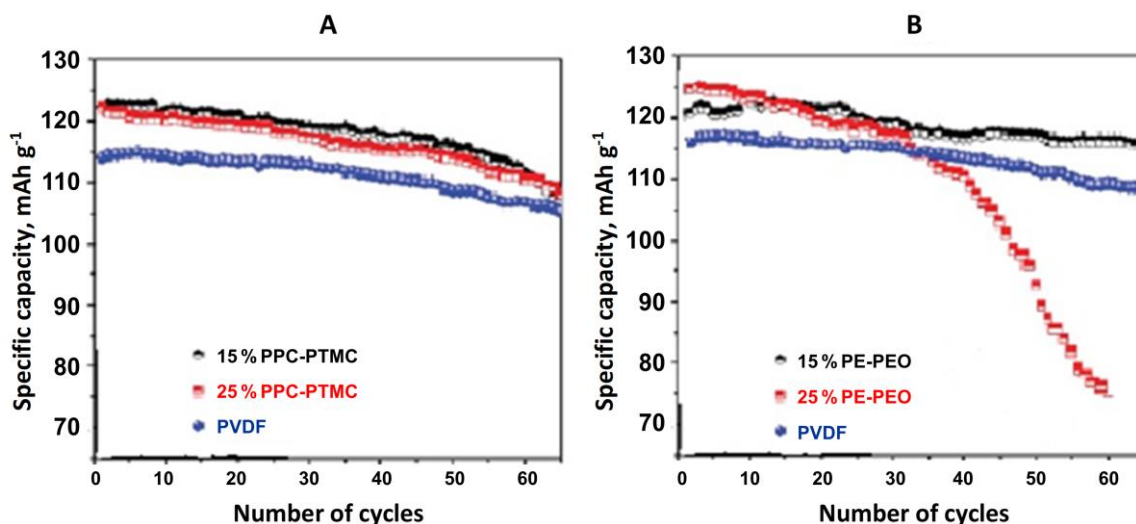


Figure 5. Electrochemical performance of PVDF blended binders

Figure 5B illustrates that the PVDF/(PE-PEO) with 25 wt.% of PE-PEO exhibits a rapid capacity loss after only 40 cycles during the cycle performance testing. This could be a result of mechanical breakdown brought by low PE-PEO molecular weight. The results of the characterization illustrated in Figure 1 enable us to correlate the dependent amounts of constituents on the mechanical and nonlinear behavior of PVDF/PEO. The PVDF/(PE-PEO) binder resulted in a 4-8 mAh g⁻¹ higher specific capacity than the PVDF cell during the course of the cycle performance tests. Compared to the PVDF/(PE-PEO) system, the electrode stability is much lower. Specifically, following cycling, the active materials even fractured when the loading of PE-PEO increased to 25 wt.%. The findings suggest that a large loading of PE-PEO causes the electrode mechanical qualities to deteriorate significantly and severely impairs the battery's electrochemical processes.

Conclusions

A straightforward copolymer mixing technique to modify PVDF binder and enhance the structural homogeneity of electrode composites is presented. As the blends of PPC-PTMC and PE-PEO are contrasted with pure PVDF binder, the dispersion and distribution of carbon black in the spinel electrode composites were enhanced. As a result of the two mixed binders, the specific capacity of the cell rises and charge transfer resistance lowers due to combination advantage. It has been noted that enhanced battery performance can only be achieved with PPC-PTMC and PE-PEO copolymer binder systems when the blended binder loading is not excessively high. Furthermore, in terms of cycle stability on higher loadings, PPC-PTMC outperforms PE-PEO as a modification of PVDF binder. The efficiency of lithium-ion migration is increased by this blending system, which offers more routes for lithium-ion transport. This evaluation offers an affordable method of managing binder function and electrochemical performance. In order to determine the anode and cathode interfacial impedances in full cells, comprehensive EIS investigations on a system-by-system basis are required for future research.

Conflicts of interest: The authors declare no conflict of interest.

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