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Optimizing the compatibility between dimethyl methylphosphonate (DMMP)-based electrolytes and carbonaceous anodes

H. F. Xiang · Q. Wang · D. Z. Wang ·
D. W. Zhang · H. H. Wang · C. H. Chen

Abstract The poor compatibility between dimethyl methylphosphonate (DMMP)-based electrolytes and carbonaceous anodes was improved by optimizing the compositions of the electrolyte and the electrode. In the electrolyte, the contents of DMMP and ethylene carbonate had significant effects on both the safety characteristic and the compatibility with carbonaceous anode. For the spherical mesocarbon microbeads, a conductive composite system containing the flake graphite and the carbon nanoparticles was beneficial to the highest reversible capacity (330 mAh g^{-1}). In the common graphite anode, the water-soluble binder was the better choice than poly(vinylidene fluoride) to suppress the reductive decomposition of DMMP. In brief, the optimized compatibility indicated an extensive prospect of the flame-retarded electrolyte in the battery industry.

Keywords Lithium-ion battery · Flame-retarded electrolyte · Water-soluble binder · Conductive additive

1 Introduction

Nowadays, lithium-ion batteries are very attractive for electric vehicles (EV), hybrid electric vehicles (HEV), and plug-in hybrid electric vehicles (PHEV) applications, owing to their high energy density and long lifetime. However, safety concern is one of the biggest barriers for the development of large-size lithium-ion batteries because of the use of the flammable electrolytes. To solve this problem, the most economic and efficient way is to use the flame-retarded electrolytes [1–8]. In the previous investigations, dimethyl methylphosphonate (DMMP) was reported as a highly efficient flame retardant for the electrolyte of the lithium-ion batteries [9–13]. The electrolyte containing 10% DMMP had good compatibility with either surface-modified graphite (SMG) or mesocarbon microbeads (MCMB) anode, even though DMMP could decompose violently on the normal graphite anode at low potential (<1 V) [9, 12]. The compatibility between the DMMP-containing electrolyte and carbonaceous anode was largely dependent on the content of DMMP. When DMMP was used as a co-solvent in the electrolyte, an "absolutely" nonflammable electrolyte with 50% DMMP could be prepared with a very high limited oxygen index (LOI) of 36, but it had poor compatibility with the SMG and MCMB anodes. Although the addition of vinyl ethylene carbonate (VEC, as a film-formation additive) had some effect on inhibiting the reductive decomposition of DMMP and the graphite exfoliation, the film-formation additive usually increased the impedance of the cells, which became flagrant especially at a high current rate or with a high content of additive (≥5%) [10]. All of these results suggest that DMMP is a promising choice for the electrolyte with high-safety characteristic, but its compatibility with carbonaceous anodes should be improved further, and definitely there is still a large space for the improvement.

From the material point of view, the compatibility between the DMMP-based electrolyte and carbonaceous

H. F. Xiang · Q. Wang · H. H. Wang
School of Chemistry & Chemical Engineering, South China University of Technology, Guangdong 510640, Guangzhou, China

D. Z. Wang · D. W. Zhang · C. H. Chen (✉)
CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Anhui 230026, Hefei, China
e-mail: cchchen@ustc.edu.cn

anode is naturally related to the chemistry of the electrolyte and the composite electrode. As for the electrolyte, the content of DMMP, the ratio of other components, and the use of film-formation additives, e.g., VEC, could have a significant impact on the compatibility. As the electrode is concerned, the nature of carbonaceous active material, the kind and content of polymeric binder, and conductive additive could also affect the compatibility. Recently, Liu et al. [14] reported that the contents of conductive additive (acetylene black, AB for short) and poly(vinylidene fluoride) (PVDF) had obvious effects on the performance of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ composite cathode. In addition, water-soluble binders have attracted the attentions of the battery industry and research communities [15–18]. Sodium carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) in the form of latex are soluble in environmentally friendly solvents, such as water, which is also welcome by battery manufacturers because of the lower cost for the novel water-soluble technology.

In this investigation, the compositions of both the DMMP-based electrolyte and the composite carbonaceous electrodes are optimized to achieve the optimal compatibility between the electrolyte and the electrode. For the DMMP-based electrolytes, an appropriate content of EC is as vital as that of DMMP for the safety characteristic and compatibility with the carbonaceous anodes. On the other hand, the effects of conductive additives and binders in two kinds of carbonaceous anodes, i.e., spherical MCMB and flake graphite (MAG10), on the compatibility with the DMMP-based electrolyte are investigated systemically. And here, the compatibility is quantitatively evaluated based on the first-cycle coulombic efficiency and reversible capacity (charge capacity) of the MCMB/Li and MAG10/Li cells, because all the cells have good cycling performance in the following cycles along with high coulombic efficiency ($\sim$100%). Herein, this investigation is not only helpful to the commercial application of the DMMP-based electrolytes but also gives a valuable clue for the studies on the other flame-retarded electrolytes, e.g., the trimethyl phosphate (TMP)-based electrolyte.

2 Experimental

As-purchased DMMP (Qingdao Lianmei Chemical Co., Ltd) was purified with a distillation step under vacuum and dried before use over molecular sieves (4A). Carbonate solvents (Guotai Huarong New Chemical Materials Co.) and LiPF$_6$ (Tianjin Jinniu Power Sources Material Co.) were used as received. VEC (Ferro, battery-grade) was used as a film-formation additive to improve the solid electrolyte interface (SEI) layer between the electrolyte and the carbonaceous anode. The electrolytes were prepared under a highly pure argon atmosphere in a glove box (MBraun Labmaster 130). All solvent ratios indicated in this article were in weight ratios.

Electrode laminates were prepared by casting a slurry containing carbonaceous material (MCMB—Shanshan Energy Materials Co. Ltd., or MAG10—Hitachi Powdered Metals Co. Ltd.), binder (PVDF, SBR and CMC), and conductive additive (AB, SuperP [SP] and graphite TIM-REX® KS6) in a certain medium (N-methyl pyrrolidone [NMP] for PVDF, deionized water for SBR and CMC) onto a copper foil. The laminates were then dried at 70 °C for 12 h in a vacuum oven, followed by being punched into discs with the diameter of 14 mm. The mass loading of active material in every disc was about 2 mg cm^{-2}. CR2032 coin cells were assembled in the glove box and then cycled on a multichannel battery cycler (Shenzhen Neware BTS2300) at the current density of 0.2 mA cm^{-2} between 0 and 3 V. The AC impedance was measured with the frequency range and the voltage amplitude set as 10 kHz–0.01 Hz and 5 mV, respectively, on a CHI electrochemical workstation.

The self-extinguishing time (SET) was measured to evaluate the flammability of the electrolytes, and a flammability diagram for the ternary solvent system (EC–DEC–DMMP) was drawn. Igniting a Q-tip that has absorbed about 0.2 g mixed solvents, we recorded the time it took for the flame to extinguish. The detailed procedures were described elsewhere [9, 19]. The morphology of the composite MCMB electrode and its components was characterized by scanning electron microscope (SEM) (JEOL JSM-6360A), and transmission electron microscope (TEM) measurement for SP nanoparticles was conducted on a JEOL 2010 FEG microscope at 200 keV.

3 Results and discussion

3.1 Compositions of the DMMP-based electrolytes

The higher content of DMMP in the electrolyte usually implies the better safety characteristics, whereas a bigger challenge on the compatibility with carbonaceous anodes must be met. A compromise between the safety characteristic and the compatibility with carbonaceous anodes seems to be ineludible at present, for the flame-retarded electrolyte. So it is significant to get the optimal electrolyte as far as both safety and compatibility are concerned. A flammability diagram of the ternary solvent system (EC–DEC–DMMP) was shown in Fig. 1 based on the flammability test of the mixed solvent systems. The *dark gray* region in the diagram is labeled to be nonflammable and the *light gray* part is self-extinguishable. Here, self-extinguishing is defined as that the solvent system can be
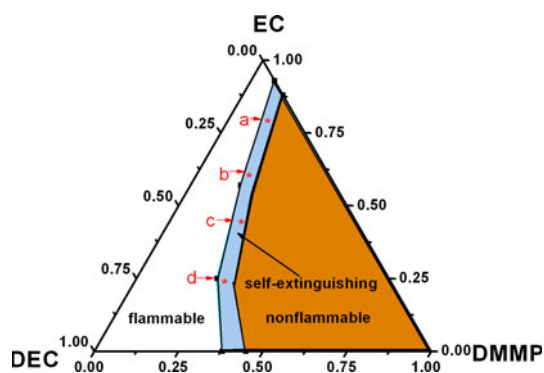
Fig. 1 The flammability diagram of ternary solvent system (EC–DEC–DMMP). Flammable: $SET > 10$ s g^{-1}; self-extinguishing: $SET < 10$ s g^{-1}; nonflammable: $SET \sim 0$ s g^{-1}

Fig. 2 The first voltage profiles of MCMB/Li cells with the DMMP-based electrolytes. **a** 1 M LiPF$_6$/EC + DEC + DMMP (80:10:10), **b** 1 M LiPF$_6$/EC + DEC + DMMP (60:25:15), **c** 1 M LiPF$_6$/EC + DEC + DMMP (45:35:20), and **d** 1 M LiPF$_6$/EC + DEC + DMMP (25:50:25). The numbers presented show the coulombic efficiency

extinguished by itself in 2 s after being ignited, that is, $SET < 10$ s g^{-1}, whereas "nonflammable" means that the solvent system cannot be ignited at all ($SET \sim 0$ s g^{-1}). The SET of the flammable electrolyte is no lower than 10 s g^{-1}. The unstable LiPF$_6$ can react with the water in air, and then the extremely toxic and corrosive gas HF is released, so here just the combustion of mixed solvent systems without LiPF$_6$ rather than the electrolytes is investigated. Actually, the electrolyte usually has slightly lower flammability than its corresponding solvent without LiPF$_6$. From Fig. 1, it is obvious that the mixed solvents keep self-extinguishing with more than 37% DMMP and nonflammable with more than 44% DMMP. When more EC is contained in the electrolyte, only less DMMP is requisite to make the ternary solvent system self-extinguishing or nonflammable. Otherwise, more DMMP is necessary for the system with more linear carbonate, DEC.

After the flammability diagram is drawn, four solvent systems in the self-extinguishing zone are used to prepare the self-extinguishing electrolytes by dissolving 1 M LiPF$_6$, i.e., (a) 1 M LiPF$_6$/EC + DEC + DMMP (80:10:10), (b) 1 M LiPF$_6$/EC + DEC + DMMP (60:25:15), (c) 1 M LiPF$_6$/EC + DEC + DMMP (45:35:20), and (d) 1 M LiPF$_6$/EC + DEC + DMMP (25:50:25). Here, the MCMB composite electrode containing 75% MCMB, 15% KS6, and 10% PVDF is used to investigate the effect of the solvent component in the electrolyte on the compatibility between the DMMP-based electrolyte and carbonaceous anode. Figure 2 shows the first-cycle voltage profiles of MCMB/Li cells with the electrolytes mentioned above. In the ternary solvent system, cyclic carbonate, EC, with a high dielectric constant, has good ability to dissolve LiPF$_6$. Above all, EC is necessary in the state-of-the-art electrolyte to form an efficient protective layer, the SEI film, which can efficiently prevent the reductive decomposition of the electrolyte on the carbonaceous anode. The linear carbonate, DEC, has a low viscosity (0.75 cP at 25 °C) and a low melting point
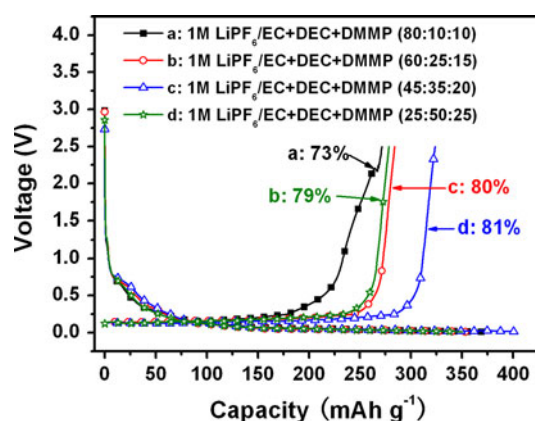
(−43 °C), which can make up the shortcomings of EC, high viscosity (1.9 cP at 40 °C), and melting point (36 °C) [20]. But DEC with a low flash point (25 °C) is very flammable; thus, more flame retardant should be used to prepare the highly safe electrolyte. As shown in Fig. 2, the MCMB/Li cell with the electrolyte (a) exhibits a low coulombic efficiency of 73% and low charge capacity, which is possibly because of the high viscosity from too much EC used. The high viscosity is adverse for Li$^+$ transfer in the electrolyte bulk and the electrolyte permeating into the porous electrode. In addition, too much EC could result in the high content of EC in the Li$^+$ solvate, and a thick SEI layer formed after reduction of the solvate above. It is easily found that the electrolyte (a) is more viscous than the other electrolytes (Fig. 2) in the experiment. With the content of EC decreasing, the performances of the cells with the electrolytes (b) and (c) are improved significantly. Especially for the electrolyte (c), the corresponding cell has a high coulombic efficiency of 81% and relatively high reversible capacity of 320 mAh g^{-1}. As for the electrolyte (d), EC is not enough to form a stable SEI layer to avoid the reductive decomposition of DMMP, so the cell performance is not as good as that of the cell with the electrolyte (c). The results of AC impedance also support the discussion above. As shown in Fig. 3, the electrolyte (a) clearly exhibits high impedance in bulk, and also the corresponding SEI interface has high impedance. For the other electrolytes, especially the electrolyte (c), all the impedances from the bulk, the interface, and charge transfer keep quite low levels. Hence, it can be deduced that EC with an appropriate content, i.e., between 30 and 60%, in the DMMP-based electrolyte, is crucial for the compatibility between the electrolyte and the carbonaceous anode.
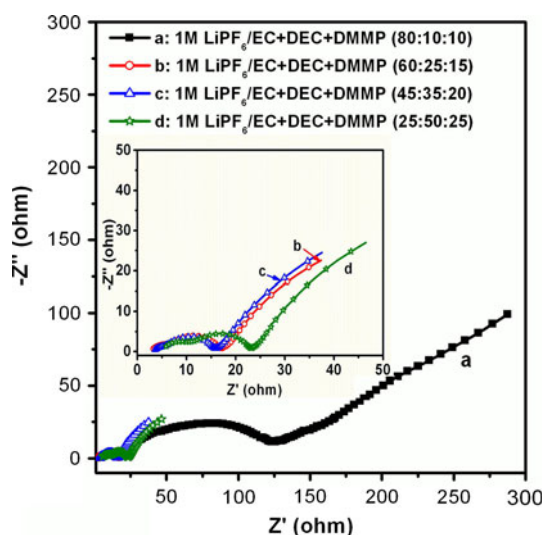
Fig. 3 AC impedance spectra of MCMB/Li cells with the DMMP-based electrolytes. **a** 1 M LiPF$_6$/EC + DEC + DMMP (80:10:10), **b** 1 M LiPF$_6$/EC + DEC + DMMP (60:25:15), **c** 1 M LiPF$_6$/EC + DEC + DMMP (45:35:20), and **d** 1 M LiPF$_6$/EC + DEC + DMMP (25:50:25). All the cells were discharged to 0.15 V after two cycles

3.2 Compatibility between the DMMP-based electrolyte and the MCMB electrode

After the electrolyte (c) with the optimal composition is chosen, the compatibility is mainly dependant on the carbonaceous anode. The MCMB electrode is usually composed of MCMB, conductive additive, and binder. Here, we systemically investigate the effects of conductive additive, binder, and their contents on the compatibility between the DMMP-based electrolyte and the MCMB electrode, as shown in Table 1. It is an orthogonal form

$L_9(3^4)$ containing three factors with three levels. There are three kinds of conductive additives, KS6, KS6-AB (1:1), and KS6-SP (1:1), and three kinds of binders, PVDF, SBR-CMC (2:1, denoted as S2C1), and SBR-CMC (5:1, denoted as S5C1). PVDF is dispersed in NMP, but the other binders are water-soluble. The contents of conductive additive and binder are designed as 15% conductive additive + 5% binder (denoted as A15B5), 15% conductive additive + 10% binder (denoted as A15B10), and 10% conductive additive + 15% binder (denoted as A10B15). The reversible capacity and coulombic efficiency of the MCMB/Li cells in the first cycle are used to evaluate the compatibility between composite anode and electrolyte. Based on the range analysis in orthogonal experimental design, the optimal condition is obtained with A3 (KS6-SP [1:1] as conductive additive), B1 (PVDF as binder), and C1 (using 15% conductive additive and 5% binder), which is helpful for both the highest reversible capacity and coulombic efficiency. The SEM images of MCMB, KS6, and the optimal electrode are shown in Fig. 4, along with the TEM image of SP. It is reasonable to believe that KS6 flakes and SP nanoparticles can cooperatively enhance the conductivity of the MCMB electrode. Both the conductive carbon materials hardly promote the reductive decomposition of DMMP. Finally, the orthogonal results have been validated by the discharge–charge testing. Figure 5 shows the first-cycle voltage profiles of MCMB/Li cells with the optimized electrode compositions. The optimized MCMB electrode with PVDF as binder clearly exhibits the reversible capacity of 330 mAh g^{-1} and the coulombic efficiency of 82%, which is definitely the optimal performance in all of the results. The water-soluble binders result in the lower reversible capacities and coulombic efficiencies than PVDF. Therefore, it can be concluded that 15%

Table 1 Orthogonal arrays for experimental design and test results

Experiment no	Factors			Results	
	A (conductive)	B (binder)	C (content)	Reversible capacity (mAh g^{-1})	Coulombic efficiency (%)
1	A1 (KS6)	B1 (PVDF)	CI (A15B5)	280	65.63
2	Al	B2 (S2C1)	C2 (A15B10)	39	55.59
3	Al	B3 (S5C1)	C3 (A10B15)	4	26.09
4	A2 (KS6-AB)	Bl	C2	148	65.96
5	A2	B2	C3	29	46.92
6	A2	B3	C1	210	76.74
7	A3 (KS6-SP)	B1	C3	187	81.98
8	A3	B2	C1	291	81.55
9	A3	B3	C2	85	67.26

In the column A (conductive), KS6-AB and KS6-SP are mixtures with the weight ratio of 1:1. In the column B (binder), S2C1 and S5C1 stand for the mixtures of SBR and CMC with the weight ratios 2:1 and 5:1, respectively. In the column C (content), A15B5 suggest that the corresponding electrode contains 15% conductive additive and 5% binder. A15B10 and A10B15 mean 15% conductive additive + 10% binder and 10% conductive additive + 15% binder, respectively
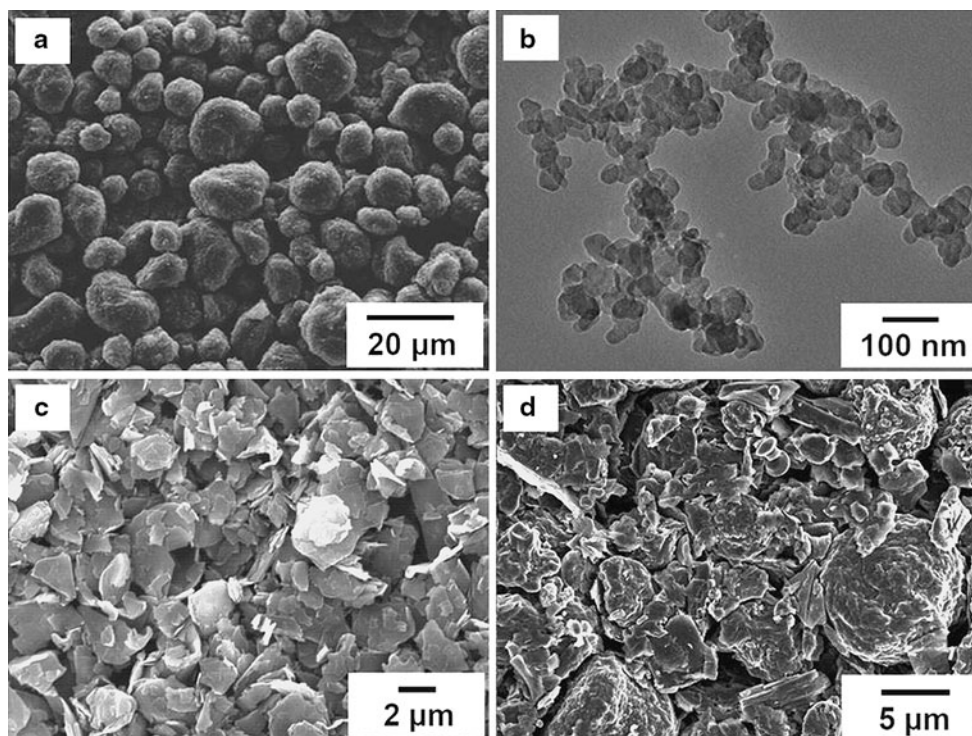
Fig. 4 SEM image of MCMB (**a**) and TEM image of SP (**b**), SEM images of KS6 (**c**), and the optimal MCMB electrode (**d**) containing 80% MCMB, 15% KS6-SP (1:1), and 5% PVDF
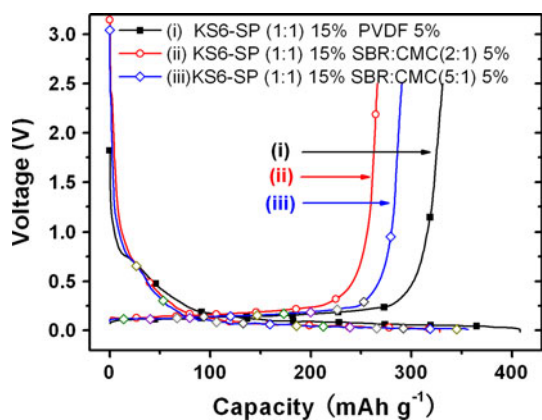

Fig. 5 The initial voltage profiles of MCMB/Li cells with the optimized electrode compositions

KS6-SP (1:1) and 5% PVDF are good choice for the excellent compatibility between the MCMB electrode and the DMMP-based electrolyte.

3.3 Compatibility between the DMMP-based electrolyte and the graphite electrode

Different with the quite stable MCMB, the flimsy graphite (MAG10) is easily exfoliated in the DMMP-containing electrolyte. Usually, it is necessary to use a film-formation additive, e.g., VEC, to protect graphite from exfoliating owing to the reductive decomposition of DMMP. Thus, an electrolyte modified by VEC, i.e., 1 M $LiPF_6$/EC + DEC + DMMP (45:35:20) + 2% VEC, is chosen for investigating the effects of various binders on compatibility between the DMMP-based electrolyte and the graphite anode. Figure 6 shows the first-cycle discharge–charge curves of the MAG10/Li cells with the DMMP-based electrolyte modified by VEC. As shown in Fig. 6a, for all the cells with 5% binder, there is a discharge plateau around 0.5 V, which is corresponding to the reductive decomposition of DMMP as reported in the literature [12]. Even though 2% VEC is added into the electrolyte as the film-formation additive, the SEI film is not stable enough to prevent the decomposition of DMMP and the resulting graphite exfoliation. Here, based on the coulombic efficiency and reversible capacity, obviously the DMMP-based electrolyte has better compatibility with the electrodes containing water-soluble binders than that using PVDF. It is widely believed that the hydroxyl groups in the CMC molecules have an active effect on the formation of SEI film [16, 21]. So the higher reversible capacity and coulombic efficiency can be obtained when the electrode contains more CMC in the binder of SBR–CMC (2:1). In most cases, 5% water-soluble binder is enough for
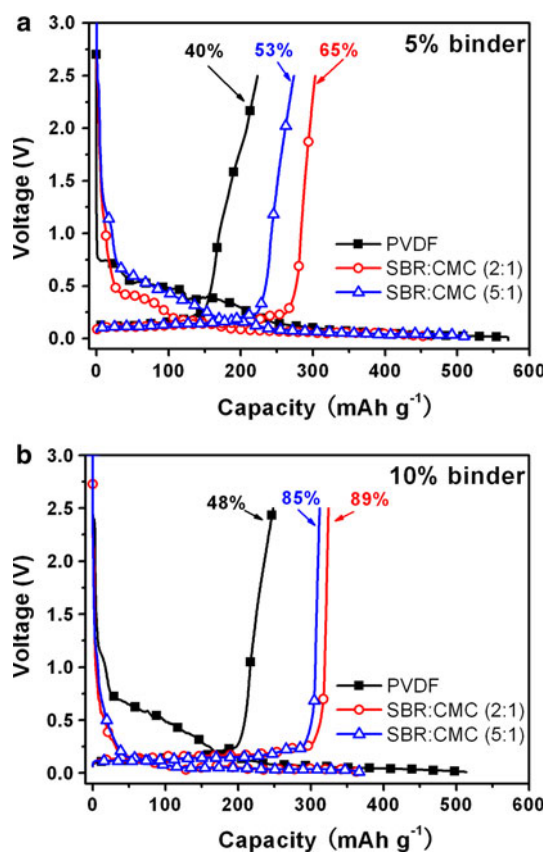
Fig. 6 The first voltage profiles of MAG10/Li cells with the electrolyte of 1 M $LiPF_6$/EC + DEC + DMMP (45:35:20) +2% VEC. The MAG10 electrodes contain 5% binder (**a**) and 10% binder (**b**), respectively. The numbers presented show the coulombic efficiency

Fig. 7 AC impedance spectra of MAG10/Li cells with the different binders: **a** PVDF, **b** SBR-CMC (2:1), and **c** SBR-CMC (5:1). The content of binder in the composite electrode is 10%. All the cells were discharged to 0.15 V after two cycles

that the water-soluble binders are contributed to the excellent SEI layer with the lower impedance (Fig. 7).

4 Conclusions

The DMMP-based electrolyte has been proved to be a promising electrolyte with high-safety characteristic, but the compatibility between this electrolyte and the carbonaceous anodes still needs to be improved. Herein, the roles of the electrolyte and the composite electrode for their compatibility have been investigated. As for the electrolyte, an appropriate ratio between EC, DEC, and DMMP is very important for the compatibility, even though the more DMMP and EC, the less DEC means higher safety characteristic. As for the spherical MCMB, it is favorable to use PVDF as the binder rather than the water-soluble SBR–CMC system. Above all, the MCMB composite electrode with the KS6-SP conductive additive exhibits the highest reversible capacity (330 mAh g^{-1}) in the DMMP-based electrolyte, probably because of the improved conductivity of the composite electrode. But for the flake graphite (MAG10), 10% water-soluble binder (SBR-CMC) is the better choice than PVDF for the formation of a stable SEI layer with lower interface impedance. In brief, the optimized compatibility between the DMMP-based electrolyte and carbonaceous anode indicates an extensive prospect of the highly safe electrolyte in the battery industry.

electrode production, owing to their better flexibility and stickiness than PVDF. But here higher content is necessary for stable SEI formed between the fragile graphite electrode and unstable DMMP-based electrolyte. As shown in Fig. 6b, the discharge plateau corresponding to the reductive decomposition of DMMP disappears after 10% water-soluble binders are used. When the binder of SBR–CMC (5:1) is used, the reversible capacity is more than 310 mAh g^{-1} and the coulombic efficiency is 85%. As for the binder of SBR–CMC (2:1), the higher reversible capacity and coulombic efficiency are obtained with 325 mAh g^{-1} and 89%, respectively, which is attributed to the stabler SEI film from the higher content of CMC. However, for the PVDF binder, there is still an obvious discharge plateau at 0.5 V corresponding to the reductive decomposition of DMMP. So it can be concluded that the water-soluble binder is helpful to improve the compatibility between the graphite anode and the DMMP-based electrolyte. In addition, the AC impedance spectra for the cells with the graphite electrodes with 10% binder indicate
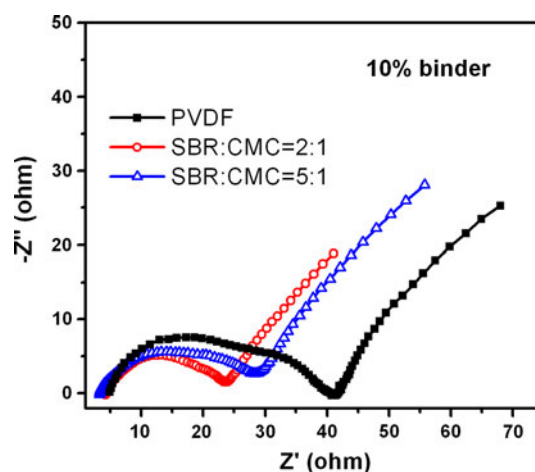
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