综述与专论

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锂离子电池用高热稳定性新型隔膜的研究新进展

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摘要： 锂离子电池以其高能量密度、长寿命、低自放电率等优点在新能源市场中得到了广泛应用。然而，锂离子电池常用的聚烯烃隔膜在高温环境下会发生皱缩和熔化，进而导致电池热失控。研制具有高热稳定性的新型隔膜有望改善电池的安全性。系统地综述了锂离子电池领域具有优异热稳定性的新型隔膜的最新研究进展，并对其设计思路以及构效关系进行了讨论，同时对上述隔膜的关键特征参数，如厚度、离子电导率、热收缩率等进行了归纳与比较。最后，对锂离子电池隔膜的未来发展方向进行了展望。

关键词： 锂离子电池；热稳定性；隔膜；聚酰亚胺；纤维素；聚偏氟乙烯-六氟丙烯
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New development of novel separators with high thermal stability for lithium-ion batteries

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Abstract: Lithium-ion batteries have been widely utilized in the new energy market due to their high energy density, long cycling life, and low self-discharge rate. However, the commonly employed polyolefin separators in lithium-ion batteries will shrink and meltdown at high temperatures, which can lead to the occurrence of battery thermal runaway. The development of novel separators with high thermal stability is expected to improve the safety of the battery. The latest research progress of new separators with excellent thermal stability in the field of lithium-ion batteries is systematically reviewed, and their design ideas and structure-activity relationship are discussed. At the same time, the key characteristic parameters of the above separators, such as thickness, ionic conductivity, thermal shrinkage, *etc*., are summarized and compared. Finally, the future development direction of lithium-ion battery separators is prospected.

Key words: lithium-ion battery; thermal stability; separator; polyimide; cellulose; polyvinylidene fluoride-hexafluoropropylene

引 言

锂离子电池由于其能量密度高、循环寿命长、环境友好等优点已经在新能源领域中广泛应用[1-4]。近年来，新能源汽车市场的蓬勃发展加快了锂离子电池技术提升的脚步。如何进一步提高电池的能量密度和功率密度以缓解人们对电动汽车的里程焦虑成为目前研究人员所关注的重点[5-7]。然而，相

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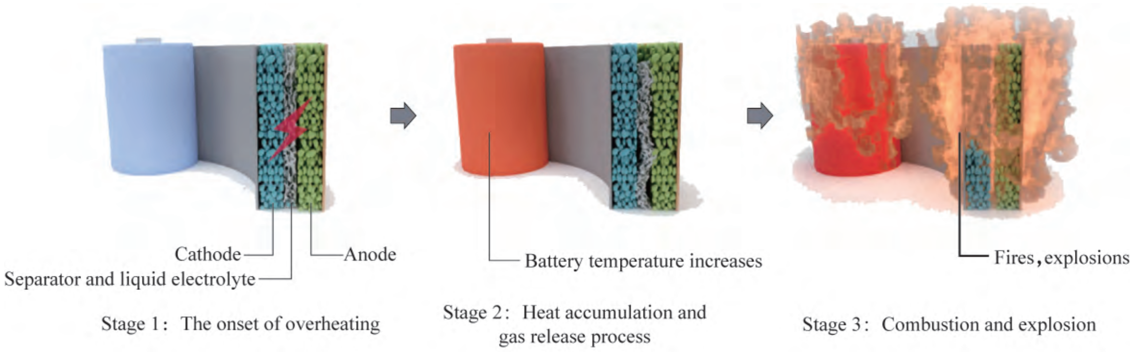
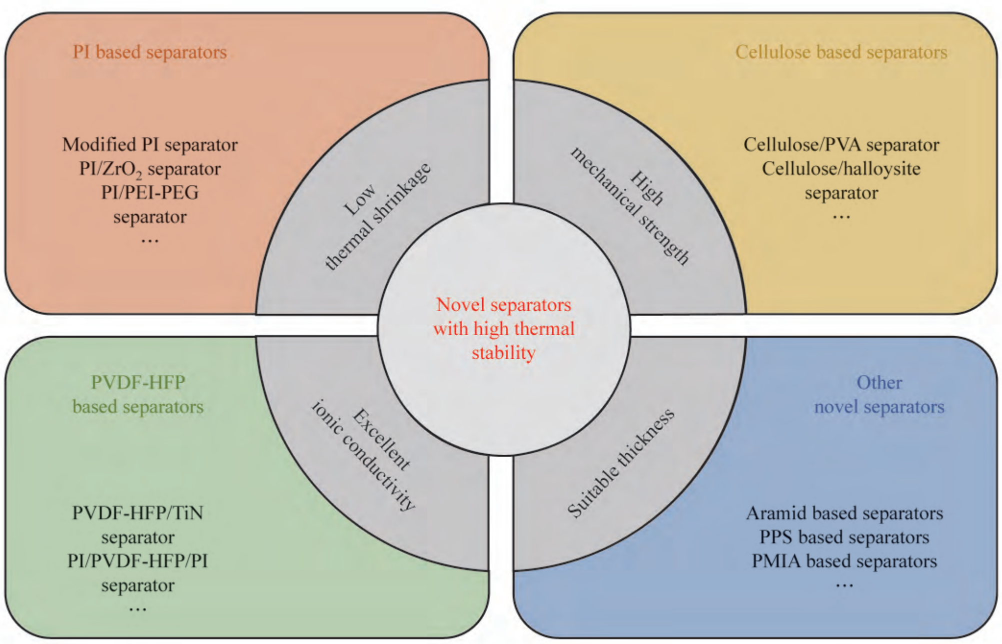
应的高电量和快速充放电的需求使得锂离子电池的安全性受到了极大的挑战。电池的电量越高，其内部的电化学反应所释放的能量越大。而快速充放电会使得电池内部反应速度加快，单位时间内产热更多，电池温度上升[8-9]。尤其在高温环境下，隔膜会发生皱缩、熔化而导致正负极直接接触，并引发电池内短路[10-12]。电池内短路会使其内部温度急剧上升，电池内部各种副反应，如负极与电解液的反应、电解液与正极结构的热分解等反应会连环发生。上述链式反应所释放的热量最终会导致电池发生热失控而起火爆炸[图1(a)]，危害公民的财产和人身安全[13-14]。

由上述讨论可知，隔膜的热稳定性直接影响电池的安全性。具有高热稳定性的隔膜会在高温下保持结构相对稳定，防止电池正负极接触；甚至在电池发生热失控过程中，通过赋予隔膜阻燃、热关闭等功能，可以延缓电池起火爆炸的发生，为消防应急处置赢得更长的反应时间[11,15]。另外，隔膜的厚度、孔隙率、离子电导率等特性对锂离子电池的安全性和电化学性能产生着较大的影响[16]。目前，常见的商业聚烯烃隔膜如聚丙烯(PP)隔膜和聚乙烯(PE)隔膜的熔点较低，其在电池热失控的初始阶段就会发生皱缩和熔化，从而进一步加快危害的发生[17]。寻找具有高热稳定性并同时兼具高机械强度、良好离子电导率等优异特性的新型隔膜材料有望改善锂离子电池的安全性问题[18-19]。基于此，本



(a)



(b)

图1 (a)锂离子电池发生热失控的过程[20]；(b)具有高热稳定性的新型隔膜的常见种类与性能要求

Fig.1 (a) The thermal runaway process of lithium-ion battery[20]; (b) Common types and performance requirements of novel separators with high thermal stability

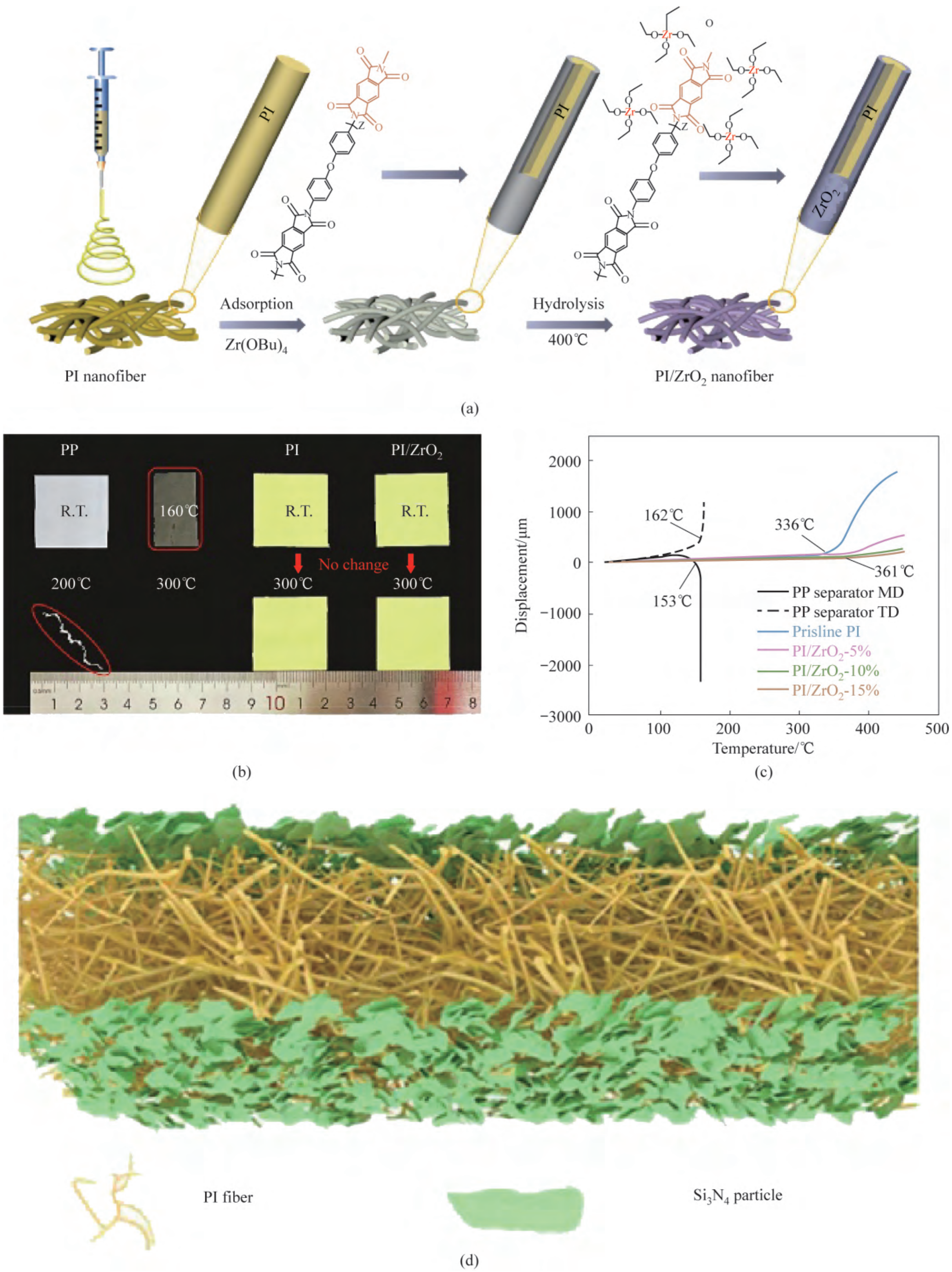
文综述了锂离子电池中具有高热稳定性的新型隔膜如聚酰亚胺(PI)基隔膜、纤维素基隔膜、聚偏氟乙烯-六氟丙烯(PVDF-HFP)基隔膜、芳纶基隔膜、聚苯硫醚(PPS)基隔膜、聚间苯二甲酰间苯二胺(PMIA)基隔膜等的最新研究进展[图1(b)],深入探讨上述隔膜的结构与性能之间的关系,同时对其制备工艺和关键特征参数,如机械强度、离子电导率、热收缩率等进行总结与比较。最后,对锂离子电池隔膜的未来发展方向进行展望。

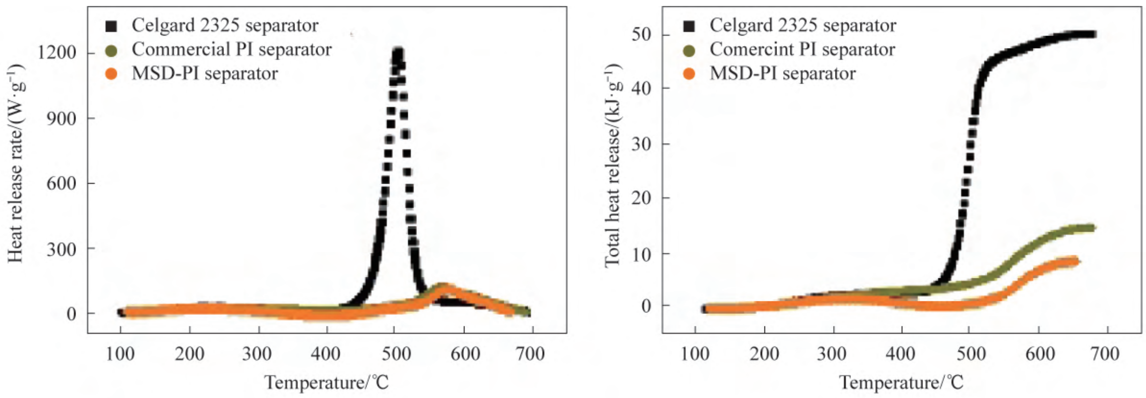
1 高热稳定性新型隔膜的研究进展

1.1 PI基隔膜

带有芳香杂环的PI作为高性能特种工程塑料,具有优异的机械强度、化学稳定性、热稳定性(分解温度大于500℃)和自熄性[24-25]。因此,PI作为隔膜基材可以很好地提高隔膜在各种滥用条件下的尺寸稳定性,从而改善锂离子电池的安全性[26-28]。Deng等[29]通过共前体法制备了一种无热亚酰化的多孔聚酰亚胺气凝胶隔膜(C-PI)。在C-PI分子结构中,2,2′-二甲基联苯胺(DMBZ)和2-氨基乙酸双乙酯(ODA)交替排列。含有ODA的PI分子链易于折叠或弯曲,而含有DMBZ的PI分子链更容易形成π-π堆积。因此,C-PI分子结构的设计保证了C-PI隔膜的抗拉强度(13.7 MPa)和柔韧性。尤其C-PI隔膜在300℃下放置0.5 h后的收缩率仅为3%,并且采用C-PI隔膜的电池的热失控温度达204.9℃,表明C-PI隔膜优异的热稳定性可有效抑制电池发生热失控。Gu等[30]通过高温缩聚反应制备了含羧基的可溶性PI,并且通过非溶剂诱导相分离得到了海绵状结构的PI隔膜。所得PI隔膜表现出高的电解液吸收率(344%),且在200℃下尺寸无明显变化。进一步地,Dang等[31]利用静电纺丝-亚酰化-碱性水解法将羧基化PI与纤维素通过氢键交联在一起制得纳米纤维复合隔膜(Cel/PI-COOH)。氢键交联形成的三维互联结构提高了Cel/PI-COOH隔膜的抗拉强度(34.2 MPa),且纤维素中丰富的羟基基团改善了Cel/PI-COOH隔膜的电解液浸润性,提高了其离子电导率(0.51 mS·cm^{-1})。更重要的是,Cel/PI-COOH隔膜展现出优异的热稳定性,在200℃下放置30 min后尺寸无收缩。相似地,Liu等[32]将纤维素纳米纤维(CNFs)与PI隔膜进行复合以改善复合隔膜的机械强度,同时加入十溴二苯乙烷(DBDPE)来改善复合隔膜的孔隙率和阻燃性。结果表明,所制备的PI/CNFs/DPDBE隔膜的孔隙率为78%,拉伸强度提高至25.4 MPa,弹性模量为550.1 MPa,并且在燃烧实验中显示出良好的阻燃性能。Sun等[33]利用聚醚酰亚胺(PEI)包覆PI纤维,并通过优化前体黏度制备了具有超高拉伸强度(95.7 MPa)和自熄能力的复合隔膜(PI/PEI)。Li等[21]采用吸附和水解策略制备了ZrO_2包覆PI复合隔膜[图2(a)]。PI/ZrO_2隔膜表现出优异的热稳定性,在300℃下外观尺寸无收缩[图2(b)]。从图2(c)的热机械分析曲线可以看出,相比于PP隔膜和原始PI隔膜,PI/ZrO_2隔膜在361℃时尺寸才出现位移,说明ZrO_2的引入进一步改善了PI基隔膜的热稳定性。Yang等[34]利用同轴静电纺丝制备出以PI为芯、PVDF-HFP为壳的复合隔膜(PI/PVDF-HFP)。PI/PVDF-HFP隔膜使得以钴酸锂为正极的电池的热失控温度提高至190℃,表明PI/PVDF-HFP隔膜能够有效改善锂电池的安全性。而Li等[35]直接将PVDF-HFP涂覆于PI隔膜表面,所得复合隔膜使得以磷酸铁锂为正极的电池在140℃下加热1 h后仍能在0.2 *C*下稳定地循环100次。Huang等[36]将聚乙二醇(PEG)化学接枝在PEI分子表面,制得一种具有高离子电导率(2.33 mS·cm^{-1})和热稳定性(200℃下放置0.5 h后尺寸无明显变化)的高性能隔膜。Liao等[22]采用磁控溅射沉积技术,在商用PI隔膜的两侧涂覆Si_3N_4,制备了具有高热稳定性的复合隔膜(MSD-PI)。微尺度燃烧量热计测量方法被用来研究了不同隔膜在燃烧时的放热指标,如热释放率(HRR)和总放热量(THR)[图2(e)]。MSD-PI隔膜的HRR峰值为97 W·g^{-1},低于Celgard隔膜(1142 W·g^{-1})和商用PI隔膜(110 W·g^{-1})。较低的HRR值可以延缓电池发生火灾事故的燃烧速度。另外,与Celgard隔膜和商用PI隔膜的THR值(50.13 kJ·g^{-1}和14.75 kJ·g^{-1})相比,MSD-PI隔膜表现出更低的THR值(8.62 kJ·g^{-1})。因此,MSD-PI隔膜能够降低电池发生热失控时的危害,保证了人员安全。Liu等[23]通过重离子轨道刻蚀技术和刮刀涂覆法制备了PI/hBN复合隔膜。如图2(f)所示,PI/hBN隔膜的底部为刻蚀后的多孔PI隔膜,而顶部涂层由紧密排列的介孔hBN纳米片组成,其有利于提高隔膜的导热性,减小隔膜的孔径。红外热成像图[图2(g)]表明,在相同加热温度下,无论采用线性热源还是点热源,PI/hBN隔膜表面温度都高于PP隔膜表面温度。PI/hBN隔膜所表现出的良好导热性可以改

善电池的散热，防止热聚集。Palanisamy等[37]利用静电纺丝技术将Al_2O_3与PI结合制备了具有高热稳定性的复合隔膜（PI-Al_2O_3）。原位多模量热分析测试表明，与商用Celgard隔膜相比，PI-Al_2O_3隔膜使得电池发生热失控的释放热量降低88%（211 $J \cdot g^{-1}$ *vs* 25 $J \cdot g^{-1}$）。有机蒙脱土[38]、无机勃姆石[39]、TiO_2[40]和SiO_2[41]等材料也被用来与PI进行复合，以进一步改善PI基隔膜的热稳定性和其他特性。表1总结归纳了近年来所报道的具有高耐热性PI基隔膜的重要特性参数，以便更好地分析比较不同改性方式及功





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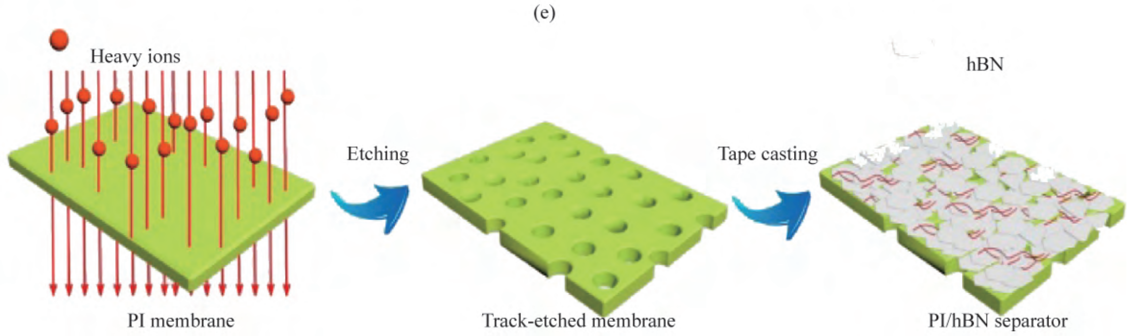

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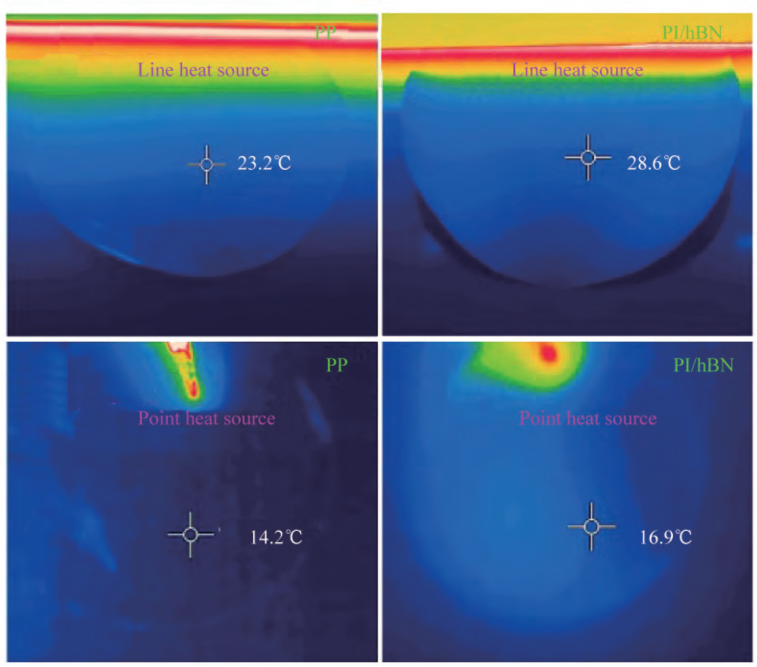


(g)

图2　(a)PI/ZrO_2隔膜的制备流程和结构示意图；(b)PP隔膜、PI隔膜和PI/ZrO_2隔膜在不同温度下热处理后的图片；(c)PP隔膜、PI隔膜和PI/ZrO_2隔膜的热机械分析(TMA)曲线[21]；(d)MSD-PI隔膜的结构示意图；(e)Celgard 2325隔膜、PI隔膜和MSD-PI隔膜的放热率和总放热量[22]；(f)PI/hBN隔膜的制备流程和结构示意图；(g)采用线热源和点热源对PP和PI/hBN隔膜进行红外热成像[23]

Fig.2　(a) Schematic diagram of the fabrication process and structure of PI/ZrO_2 separator; (b) Photographs of PP separator, PI separator and PI/ZrO_2 separator after heat treatment at different temperatures; (c) Thermal mechanical analysis (TMA) curves of PP separator, PI separator and PI/ZrO_2 separator[21]; (d) Schematic structure of MSD-PI separator; (e) Heat release rate and total heat release curves of Celgard 2325 separator, PI separator and MSD-PI separator[22]; (f) Schematic diagram of the fabrication process and structure of PI/hBN separator; (g) Infrared thermal images of PP separator and PI/hBN separator using a line heat source and a point heat source[23]

表1 PI基隔膜的物理化学特性

Table 1 Physicochemical properties of PI based separators

Material	Preparation method	Thickness/μm	Tensile strength/MPa	Porosity/%	Ionic conductivity/(mS·cm^{-1})	Electrolyte uptake/%	Thermal shrinkage/%	Ref.
PI/CNFs/DPDBE	casting	18	25.4	78	0.45	192	0 (200℃, 1 h)	[32]
PVDF-HFP@PI	electrospinning	22	—	80	1.79	800	0 (140℃, 0.5 h)	[35]
PI/PEI-PEG	impregnation	28	39	66.4	2.33	168	—(200℃, 0.5 h)	[36]
Si_3N_4/PI	casting	约48	18.2	72.2	0.66	180	—(400℃, 1 h)	[42]
PI/PVDF-HFP	electrospinning	25	19	86.7	1.24	366.6	—(400℃, 0.5 h)	[34]
cross-linked PI	electrospinning	24	—	81	1.1	540.2	—(250℃, 1 h)	[43]
PI/PEI	electrospinning	12.3	95.7	75	1.42	210.6	—(200℃, 0.5 h)	[33]
PI/montmorillonite	electrospinning	50	14.7	72	0.77	1615	—(250℃, 0.5 h)	[38]
PI/hBN	ion etching and coating	14	220.1	44.5	—	62.7	0 (280℃, 0.5 h)	[23]
PI/ZrO_2	electrospinning and pyrolysis	33	25.7	86	1.32	456	0 (300℃, —)	[21]
PI/AlOOH	impregnation	31.7	35.21	80	2.04	392	0 (250℃, —)	[39]
PI containing carboxyl groups	casting	26	16.55	75.2	0.717	344	0 (200℃, —)	[30]
TiO_2@PI	electrospinning	26.5	—	89.1	2.52	721	—(160℃, 0.5 h)	[44]
PI aerogel	casting	—	13.7	74.38	0.524	329.1	约3 (300℃, 0.5 h)	[29]
cellulose/carboxylated PI	electrospinning and pyrolysis	20	34.2	78	0.51	638	0 (200℃, 0.5 h)	[31]
PI/SiO_2	electrospinning and pyrolysis	19	73.69	61	1.55	264	0 (200℃, —)	[45]
PI/A-POSS	electrospinning	41	13.58	83.8	2.617	1149	—(280℃, —)	[46]
Si_3N_4/PI/Si_3N_4	magnetron sputtering deposition	21.4	—	61.35	0.6631	321.66	0 (200℃, 0.5 h)	[22]
PI/PAALi	electrospinning and impregnation	40	16.1	67.6	1.37	—	0 (160℃, 0.5 h)	[47]

能性材料对其物理化学特性的影响。

1.2 纤维素基隔膜

纤维素作为一种资源丰富的可再生材料，具有低成本、环境友好（无毒、可降解）、良好耐受性和电解液润湿性等特点。将纤维素与高机械强度、高耐热性材料复合以制备具有优异热稳定性的先进隔膜可有效提升电池的安全性[50-51]。Zhang等[52]利用热稳定性良好的芳纶纳米纤维（ANFs）改善了纤维素基隔膜孔径大、机械强度低、易燃性高等缺陷。结果显示，含20%（质量分数）ANFs的复合隔膜（CF/ANF-20）具有优异的耐热性（在200℃下放置0.5 h后无收缩）和阻燃性，能够保证电池的安全运行。Zou等[53]通过微纳层共挤出技术制备了聚丙烯纳米带/纤维素复合隔膜（PPNBs/CS）。聚丙烯纳米带作为支撑骨架可提高纤维素隔膜的机械强度和热稳定性，并优化其孔径大小和孔隙率。Wang等[54]利用溶胶-凝胶法制备了一种均匀多孔的纤维素纳米纤维/硅酸镁锂复合隔膜（CLP），同时PEG被用作非离子表面活性剂来调节纤维素与硅酸镁锂之间的界面相容性，使其分布均匀。结果显示，CLP隔膜具有优异的热稳定性（在200℃下放置0.5 h后无收缩）、高孔隙率（68%）和高离子电导率（0.977 mS·cm^{-1}）。另外，得益于HAP良好的耐热性，HAP/纤维素复合隔膜被设计制备，并表现出出色的热稳定性（在250℃下放置0.5 h后无收缩）和阻燃性能[55]。

将接枝或包覆技术应用到设计耐高温的纤维素基隔膜中，可防止隔膜中高热稳定性材料脱落。Fu等[48]通过超声和冷冻干燥法将十溴二苯乙烷（DBDPE）阻燃剂包裹在二维纤维素纳米片自滚形成的微卷中[图3(a)]，然后将所得混合物超声分散到去离子水中，过滤得到湿膜，并在无水乙醇中浸泡24 h，最后真空干燥得到复合隔膜（Cel@DBDPE）。红外热成像仪记录了PP隔膜和Cel@DBDPE隔膜随温度升高过程中的温度与外观尺寸变化。如图3(b)所示，PP隔膜的表面温度与环境温度接近，而Cel@DBDPE隔膜的表面温度始终低于环境温度。同时，PP隔膜在120℃时呈现收缩趋势，当温度升高到180℃时，收缩到近乎消失。相比之下，Cel@DBDPE隔膜尺寸无明显变化，表明其具有优异的热稳定性。其次，即使电池发生着火，Cel@DBDPE隔膜也会释放出Br·，Br·会与电解液燃烧产生的H·和OH·发生反应，通过自由基清除机制

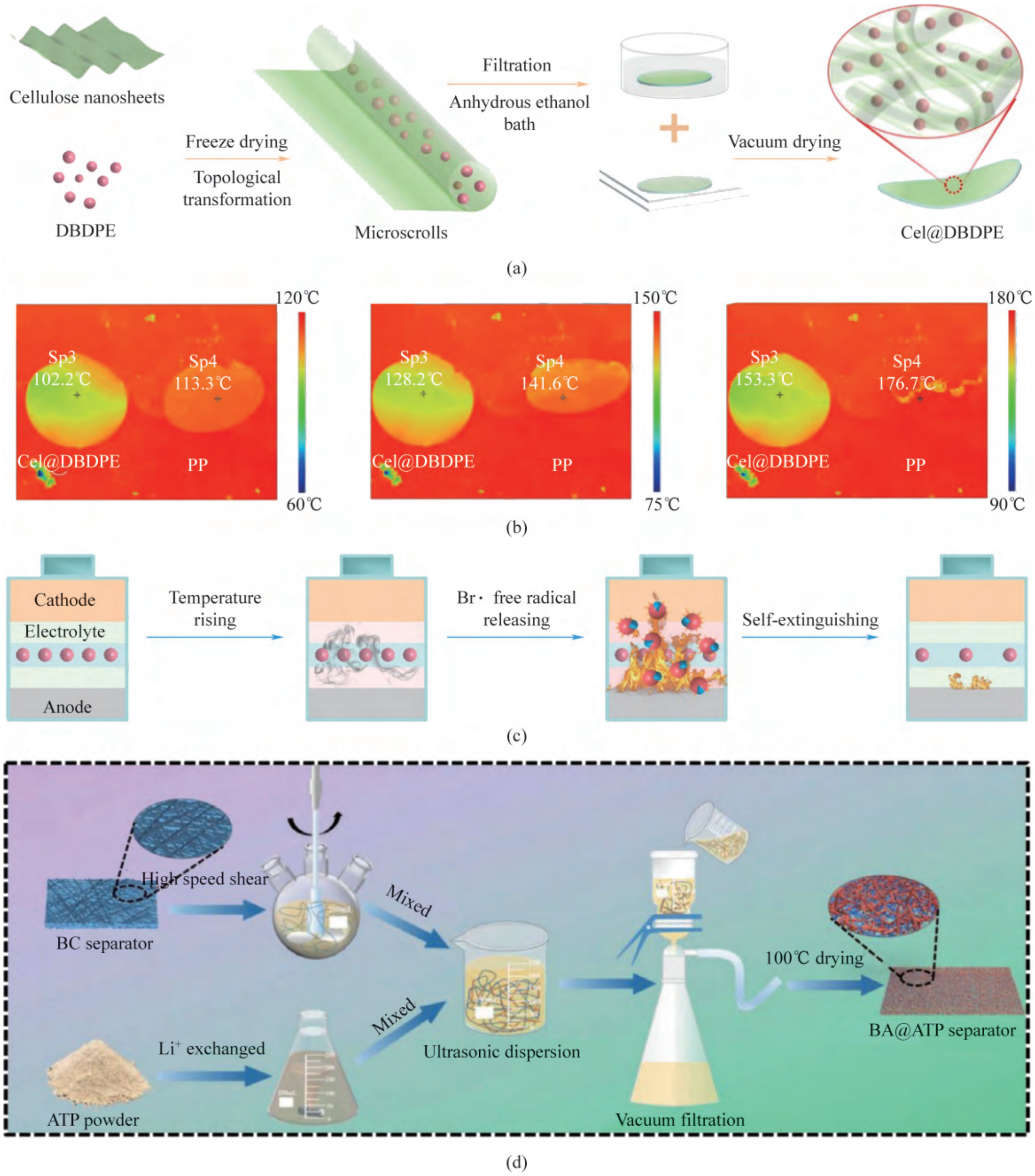


图3 (a)Cel@DBDPE隔膜的制备流程及结构示意图；(b)Cel@DBDPE隔膜和PP隔膜在不同温度下红外成像图；(c)Cel@DBDPE隔膜的阻燃机理[48]；(d)BA@ATP隔膜的制备流程及结构示意图[49]

Fig.3 (a) Schematic diagram of the fabrication process and structure of Cel@DBDPE separator; (b) Infrared thermal images of Cel@DBDPE separator and PP separator at different temperatures; (c) Flame retardant mechanism of Cel@DBDPE separator[48]; (d) Schematic diagram of the fabrication process and structure of BA@ATP separator[49]

扑灭电解质的燃烧[图3(c)]。因此，具有优异热稳定性和阻燃性能的Cel@BDBDPE隔膜可以有效提高锂离子电池的安全性。Liu等[56]将9,10-二氢-9-氧杂-10-磷杂菲-10-氧化物(DOPO)和肉桂酰氯接枝在纤维素的主链上，并通过相转化法制备了具有阻燃功能的复合隔膜(DCC)。相比于PP隔膜，DCC隔膜在放热速率和放热总量方面显著降低。Miao等[57]利用分子间氢键作用制备了PVA/纤维素复合隔膜(P-CMs)。P-CMs隔膜表现出良好的热稳定性(在300℃下放置0.5 h后其尺寸无可见变化)，且交联形成的三维网状多孔结构更有利于电解液的浸润和锂离子的扩散。Delaporte等[58]在氧化铝表面接枝了卤素基和磷基分子，然后将其掺入到纤维素隔膜的孔隙中。热重实验和火焰实验表明，在纤维素基体中使用阻燃性陶瓷材料是提高隔膜热稳定性，减缓甚至避免其燃烧的有效方法。

以市场上已广泛应用的纤维素材料(如面巾纸、报纸、A4纸等)为基材制备具有高热稳定性的隔膜可显著降低成本,易于规模化。Hu等[59]通过聚(二甲基硅氧烷)二缩水甘油醚(PDMSDGE)、PVDF-HFP和PEI依次反应,在挤压处理的面巾纸表面制得一种双交联涂层,以改善其孔隙率、电解液润湿性、力学强度以及耐热性能。Huang等[60]在商业纸和废旧报纸的两面涂覆天然高岭土纳米管,以制备高热稳定性的复合隔膜(HNTs@A4)。HNTs@A4隔膜在火中燃烧或在200℃下放置0.5 h后外观与结构无明显变化,且热处理后的HNTs@A4隔膜所组装的电池可正常运行,这表明HNTs@A4隔膜可有效提升电池的安全性。Raja等[61-62]在商业纸表面分别涂覆$BaTiO_3$和SiO_2纳米颗粒,所得到的复合隔膜在200℃下外观尺寸均保持稳定。

纤维素主要来源于天然植物,如木材。随着科学技术的发展,由微生物细菌发酵合成的多孔网状聚合物——细菌纤维素,受到人们的关注[63]。与植物纤维素相比,细菌纤维素成膜后具有更高的拉伸强度和孔隙率。Liao等[49]利用干法造纸技术制备了一种成本低、离子电导率高、阻燃性能优异的环保型细菌纤维素(BC)与凹凸棒土(ATP)复合隔膜(BA@ATP)。如图3(d)所示,为破坏低孔隙率BC隔膜的致密结构,采用高速均质机打破纤维排列顺序,并与中空ATP相结合,最后通过抽滤、干燥过程得到BA@ATP隔膜。BA@ATP隔膜在点燃后具有自熄特性,在燃烧状态下释放出极低的热量和烟气。另外,含有BA@ATP隔膜的软包锂离子电池在燃烧时表现出更高的自热温度以及更低的热释放率和总热释放值,表明电池的安全性得到了提高。Zhang等[64]将聚磷酸铵(APP)与木质素磺酸盐和聚酰胺-环氧氯丙烷(LPC)引入到BC中。BC、LPC和APP分子间的氢键作用力和共价交联作用力增强了所制备的复合隔膜(BLA)的机械强度,同时APP提升了BLA隔膜的阻燃性能。其他材料如氮化硼(BN)气凝胶[65]、ZIF-8[66]等也被研究与BC相结合,并且所得复合隔膜均表现出优异的热稳定性。表2系统梳理了近年来相关文献报道中具备卓越热稳定性的纤维素基隔膜的关键性能指标,以深入了解不同改性策略与功能材料对其物理化学特性的影响。

1.3 PVDF-HFP基隔膜

PVDF-HFP作为一种常见的PVDF共聚物,具

表2 纤维素基隔膜的物理化学特性

Table 2 Physicochemical properties of cellulose based separators

Material	Preparation method	Thickness/μm	Tensile strength/MPa	Porosity/%	Ionic conductivity/($mS\cdot cm^{-1}$)	Electrolyte uptake/%	Thermal shrinkage/%	Ref.
cellulose/PPNBs	co-extrusion	20	50	78.4	1.04	326	30 (260℃, —)	[53]
cellulose/APP/LPC	casting	85	12.9	70	2.45	446	0 (210℃, 1 h)	[64]
cellulose/PVA	casting and impregnation	45	50.1	63.3	1.81	397	—(300℃, 0.5 h)	[57]
cellulose/hydroxyapatite	filtration	28	9.94	76	0.81	162	0 (250℃, 0.5 h)	[55]
cellulose/DBDPE	filtration	15	20	—	0.27	244	0 (210℃, —)	[48]
cellulose/PVDF/$BaTiO_3$/SBR	sizing, impregnation and lamination	20	50.15	—	0.19	270.21	0 (200℃, —)	[67]
ZIF-8@cellulose/ANFs	filtration and extrusion	—	70.7	62.4	1.6	267.8	—(200℃, 0.5 h)	[66]
cellulose/ANFs	filtration and extrusion	40	33	49.5	0.75	157.4	0 (200℃, 0.5 h)	[52]
cellulose/PVDF-HFP/PEI/SiO_2	impregnation	49	9.9	71	0.69	254	0 (250℃, 1 h)	[68]
cellulose/chitosan/PVA/$BaTiO_3$	coating	70	41.31	—	—	约140	0 (200℃, 0.167 h)	[61]
cellulose/attapulgite	filtration	—	3.71	58.08	1.734	470.03	0 (250℃, —)	[49]
cellulose/halloysite nanotubes	coating	120	20.1	76.8	0.42	295	—(200℃, 0.5 h)	[60]
cellulose/PVDF-HFP/PEI/PDMSDGE	impregnation	55	19.9	70	0.59	230	—(200℃, 1 h)	[59]
cellulose	filtration	—	45.3	61.5	1.08	225.8	0 (160℃, 0.167 h)	[69]
cellulose/chitosan/PVA/SiO_2	coating	70	34.86	—	0.58	147	0 (200℃, —)	[62]
cellulose/laponite/PEG	dry	—	143.3	68	0.977	260	0 (200℃, 0.5 h)	[54]
cellulose	filtration	35	49	63.4	0.71	136.4	0 (150℃, 0.5 h)	[70]

有更优异的亲水性、耐高温性、耐候性以及绝缘性能[73]。然而,PVDF-HFP成膜后韧性较差。基于此,Parsaei等[74]采用静电纺丝法制备了PI/PVDF-HFP/PI三明治型隔膜,并对其进行压制和热处理。压制和热处理提高了PI/PVDF-HFP/PI隔膜的孔隙率(71.57%)、拉伸强度(19.09 MPa)和热稳定性(在220℃下放置1 h后的热收缩率为2%)。Kim等[75]采用相转化法制备了PVDF-HFP/甲基磷酸二甲酯(Fyrol DMMP)复合隔膜。PVDF-HFP/Fyrol DMMP隔膜表现出比商业PP隔膜高近10倍的电解液吸收率(2213%)。另外,PVDF-HFP/Fyrol DMMP隔膜在燃烧实验中多次点火,均迅速熄灭(<1.0 s),展现出优异的阻燃性能。相似地,Han等[76]将三聚氰胺焦磷酸盐(MPP)与PVDF-HFP结合制备的复合隔膜在点火实验中的熄火时间仅为0.54 s,比商业PP隔膜缩短了74.4%。然而,大部分磷基阻燃剂会钝化负极表面,导致电池的电化学性能下降。因此,Zhang等[71]将乙氧基化三羟甲基丙烷三丙烯酸酯(TMPETA)与烯丙基磷酸二乙酯(DEAP)接枝在PVDF-HFP表面,制备了一种智能温度响应的阻燃隔膜(TPF),如图4(a)所示。在电池正常运行时,DEAP与聚合物骨架共价结合紧密,不会释放出对电池电化学性能不利的含磷分子。当电池温度升高到90℃时,TPF聚合物自动释放含磷自由基,抑制放热链式反应,延缓电池热失控的发生[图4(b)]。ARC曲线[图4(c)]表明两种电池在外部加热约15 h后开始自加热(自加热温度,T_s)。采用Al_2O_3-Celgard隔膜的电池经过8.9 h的自加热后达到最高温度(T_{max})并发生热失控。相比之下,TPF膜的T_{max}降低了约30℃,并显著地延迟了电池发生热失控的时间。根据TG曲线和DSC曲线[图4(d)]分析,TPF膜在约87℃时开始失重(释放含磷自由基[PO]·)。在整个电池自加热过程(100~200℃)中,TPF膜不断释放[PO]·,清除在高温下有机电解质和高镍正极热分解产生的高活性自由基(H·、HO·和O·)。相比之下,PE隔膜在约140℃处出现一个尖峰,表明PE隔膜发生熔毁。PE隔膜熔毁会引起内部短路,进一步产生热量,加剧电池的热失控。基于ARC曲线和热分析曲线,绘制1.8 Ah软包电池在使用Al_2O_3-Celgard隔膜和TPF膜时的温度-时间轴[图4(e)]。与Al_2O_3-Celgard隔膜相比,TPF膜可以有效延缓电池内部温度上升,为电池的安全管理提供了17.8 h的关键时间窗口。Long等[77]采用流延法,将纳米$CaCO_3$引入到PVDF-HFP基体中,制备了PVDF-HFP/$CaCO_3$复合隔膜(CPVH)。CPVH隔膜表现出优异的热稳定性(300℃下放置1 h尺寸无变化)、阻燃性和低的放热量(约为PP的11%)。另外,$CaCO_3$可以中和电解液中的HF,保证了电极界面层的稳定性。因此,采用CPVH隔膜的电池在120℃下以2*C*的倍率循环100次后的容量保持率可达78.4%。Zhao等[78-79]分别将TiN和SiC与PVDF-HFP相结合,制备出两种机械强度高、热稳定性能好并可以有效抑制锂枝晶形成的复合隔膜。Hou等[72]将HAP纳米线、MXene和PVDF-HFP三者相结合,制备出安全性能更高的M-HAP@PVHF复合隔膜,如图4(f)所示。M-HAP@PVHF隔膜可以在锂负极表面生成稳定的LiF层,均匀化锂离子的沉积行为,从而抑制锂枝晶的形成,同时在火焰中能保持其初始形态和尺寸,从而双重保证电池的安全性。表3系统归纳了近年来所报道的具有优异热稳定性的PVDF-HFP

表3 PVDF-HFP基隔膜的物理化学特性

Table 3 Physicochemical properties of PVDF-HFP-based separators

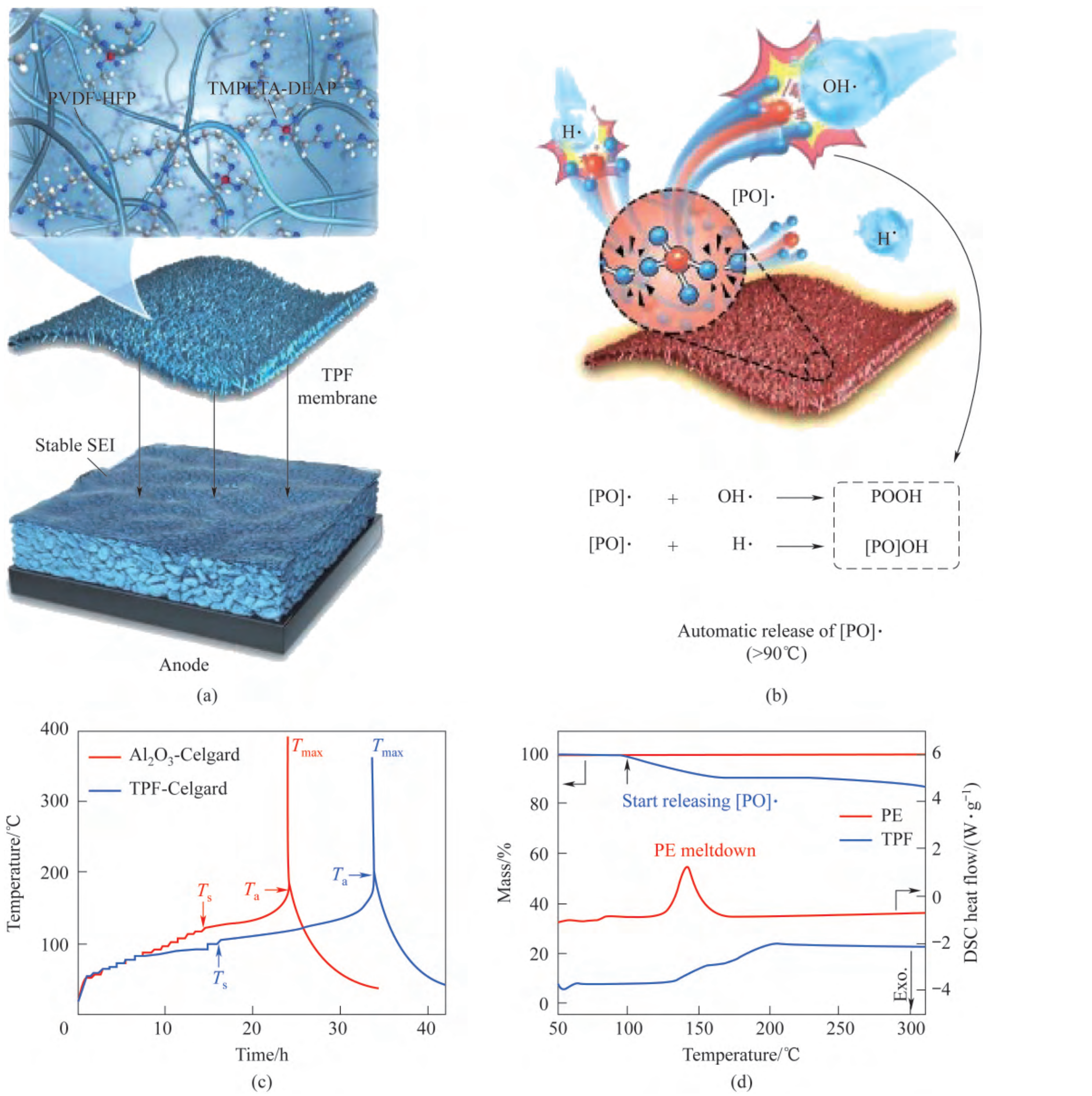
Material	Preparation method	Thickness/μm	Tensile strength/MPa	Porosity/%	Ionic conductivity/($mS\cdot cm^{-1}$)	Electrolyte uptake/%	Thermal shrinkage/%	Ref.
PVDF-HFP/TiN	casting	25	12.1	—	1.02	192	约6 (175℃, 1 h)	[78]
PVDF-HFP/SiC	casting	—	14.6	—	1.32	249	5 (150℃, 1 h)	[79]
PVDF-HFP/TPP	casting	约35	—	—	0.28	115.2	15 (140℃, 0.5 h)	[80]
PVDF-HFP/Fyrol DMMP	casting	25	—	约48.9	—	2213	0 (220℃, 0.5 h)	[75]
PVDF-HFP/MPP	casting	25	—	44.6	0.327	429.4	—(200℃, 0.5 h)	[76]
PVDF-HFP/TMPETA-DEAP	casting	44	—	—	2.8	—	约2 (160℃, —)	[71]
PI/PVDF-HFP/PI	electrospinning, extrusion and heat	46	19.09	71.57	1.23	529	2 (220℃, 1 h)	[74]
PVDF-HFP/$CaCO_3$	casting	20	3	—	0.18	约113	0 (300℃, 1 h)	[77]
PVDF-HFP/Si_3N_4	casting	72	3.13	75.2	0.884	230	—(200℃, —)	[81]

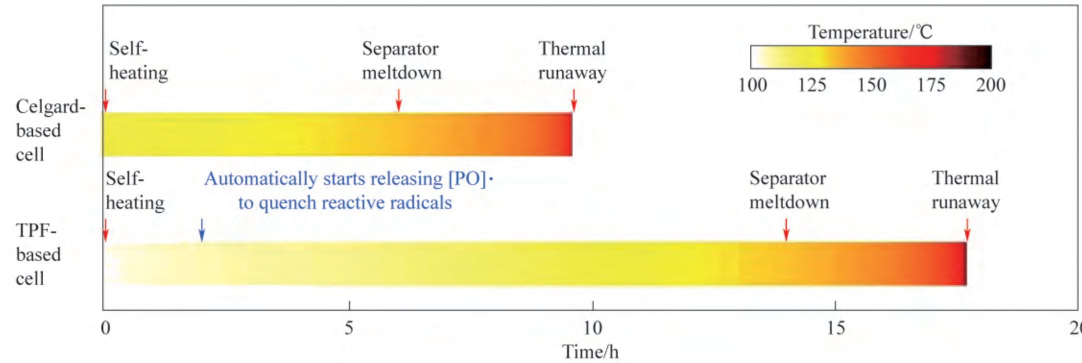
基隔膜的关键性能指标，以便更好地分析比较不同改性方式及功能性材料对PVDF-HFP基隔膜理化特性的调控规律。

1.4 其他种类隔膜

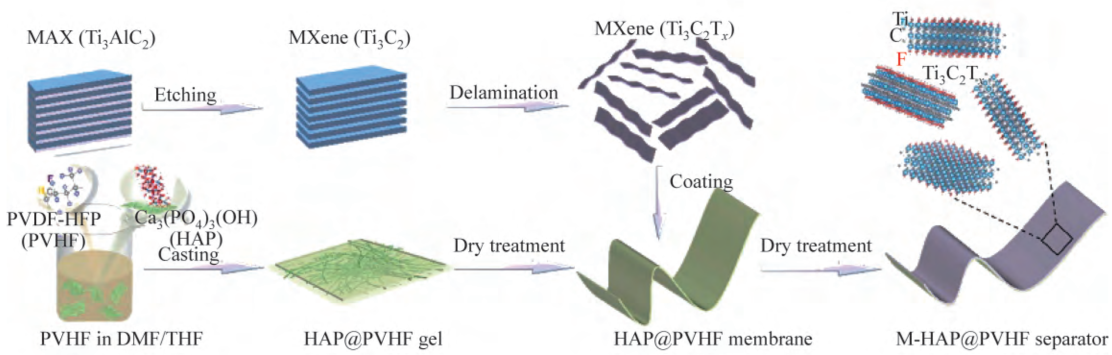
聚芳基醚苯并咪唑(OPBI)是一种具有咪唑基团的芳香族聚合物。得益于其本征阻燃性、良好的力学性能和高的化学稳定性，OPBI被用作隔膜材料，可有效地提高电池的安全性。Liu等[82]采用流延法制备了金属有机框架(MOF)/OPBI复合隔膜(UiO-66@OPBI)，如图5(a)所示。OPBI的多孔结构与MOF的离子通道形成了互联的多孔网络结构，实现了更高的离子电导率(1.74 mS·cm^{-1})。同时，UiO-66@OPBI隔膜表现出良好的阻燃特性(卷曲而不燃烧)。Min等[87]又将共价有机框架(COF)引入到OPBI基体中，制备了OPBI@COF复合隔膜。COF的加入提高了OPBI隔膜的电解液吸收率(从308%到428%)，因此隔膜的离子电导率得到了改善(从0.873 mS·cm^{-1}到1.214 mS·cm^{-1})。进一步地，磺化的COF材料(SCOF)与OPBI相结合制备出SCOF@OPBI复合隔膜[88]。SCOF的均匀孔隙和极性磺酸基团增强了锂离子的传导(1.76 mS·cm^{-1})，同时促进了锂离子的均匀沉积，抑制了锂枝晶的形成。更重要的是，SCOF@OPBI隔膜在200℃下放置1 h后尺寸无变化，说明其具有优异的热稳定性。

芳纶纤维由于其丰富的芳香基团和极性酰胺基团而表现出优异的机械强度和柔韧性、良好的电解液亲和力以及高的热稳定性。Liu等[83]以芳纶纳米纤维(ANFs)为基体制备了ANFs气凝胶隔膜。在高温下，ANFs隔膜表现出良好的热稳定性(在300℃下放置1 h后无收缩)和阻燃特性。因此，在90℃的





(e)



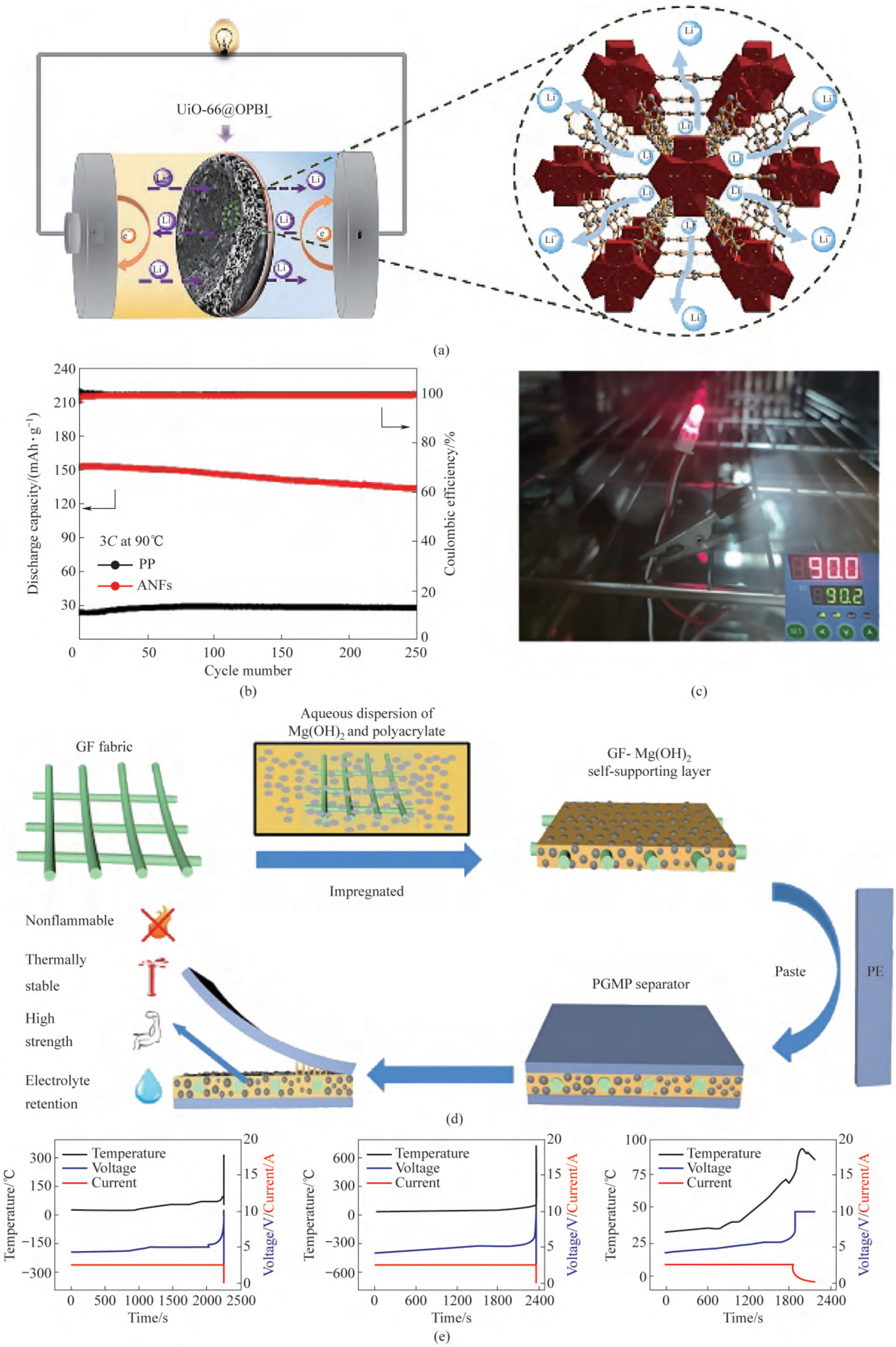
(f)

图4 TPF膜的结构示意图(a)和阻燃机理(b);(c)采用Al_2O_3-Celgard隔膜和TPF隔膜的软包电池的ARC曲线;(d)PE隔膜及TPF隔膜的热重(TG)曲线和DSC曲线;(e)采用Al_2O_3-Celgard隔膜和TPF隔膜的软包电池发生自加热后的温度-时间轴[71];(f)M-HAP@PVHF隔膜的制备流程及结构示意图[72]

Fig.4 Structure diagram (a) and flame retardant mechanism (b) of TPF separator; (C) ARC profiles of pouch cells with Al_2O_3-Celgard separator and TPF separator; (d) Thermogravimetry (TG) and DSC profiles of PE separator and TPF separator; (e) Temperature-time axis after self-heating of pouch cells with Al_2O_3-Celgard separator and TPF separator[71]; (f) Schematic diagram of the fabrication process and structure of M-HAP@PVHF separator[72]

工作温度下,采用ANFs隔膜的电池在3*C*下能够稳定循环200次[图5(b)],且能够维持一个灯泡在高温下长时间工作[图5(c)]。Parekh等[89]利用真空辅助自组装法制备了ANFs隔膜,并通过临界点干燥(CPD)工艺对其进行干燥。CPD工艺保留了隔膜的孔隙结构,改善了隔膜对电解液的润湿性。另外,所制备的CPD-ANF隔膜表现出优异的热稳定性,温度升高至350℃时无热行为,并且在300℃下经过多模块量热法测试后,其尺寸也保持基本完整。Zhang等[90]通过真空抽滤法将沸石咪唑骨架-8(ZIF-8)与ANFs相结合,制备出ZIF-8/ANFs复合隔膜。ZIF-8颗粒防止了ANFs的致密堆积,将隔膜的孔隙率从23.8%提升至61.6%,因而其离子电导率得到了提升。另外,由于ANFs和ZIF-8的阻燃特性,ZIF-8/ANFs隔膜在燃烧实验中表现出良好的自熄性。纤维素纳米纤维[91]与环氧乙烷[92]也被研究与ANFs相结合制备出具有优异耐热性和阻燃性的功能性隔膜,以保证电池的稳定运行与危险最小化。

玻璃纤维(GF)作为一种高性能无机非金属材料,具有高的拉伸强度、良好的热稳定性、低成本、资源丰富等优点。Chen等[84]开发了一种PE/GF-$Mg(OH)_2$/PE复合隔膜(PGMP),如图5(d)所示。将GF织物基材浸入到聚丙烯酸酯和$Mg(OH)_2$的混合分散液中,并在GF两侧依次黏合PE微孔膜,最终得到PGMP隔膜。与PE隔膜相比,PGMP隔膜具有更高的机械强度、离子电导率和电解液浸润性。此外,PGMP隔膜在350℃下放置0.5 h后尺寸几乎无收缩。图5(e)展示了在过充电实验中,采用不同隔膜的电池的温度、电压和电流变化。结果表明,在电压达到5 V之前,使用PE隔膜或PGP隔膜[无$Mg(OH)_2$]的电池的温度变化缓慢。但当电压达到5 V时,电池的升温速度开始加快,这可能与电池内部材料在


UiO-66@OPBI
Li
e
(a)
Discharge capacity/(mAh·g^{-1})
Coulombic efficiency/%
3C at 90℃
PP
ANFs
Cycle number
(b)
90.0
90.2
(c)
GF fabric
Aqueous dispersion of $Mg(OH)_2$ and polyacrylate
GF- $Mg(OH)_2$ self-supporting layer
Impregnated
Paste
PE
PGMP separator
Nonflammable
Thermally stable
High strength
Electrolyte retention
(d)
Temperature
Voltage
Current
Temperature/℃
Voltage/V/Current/A
Time/s
(e)

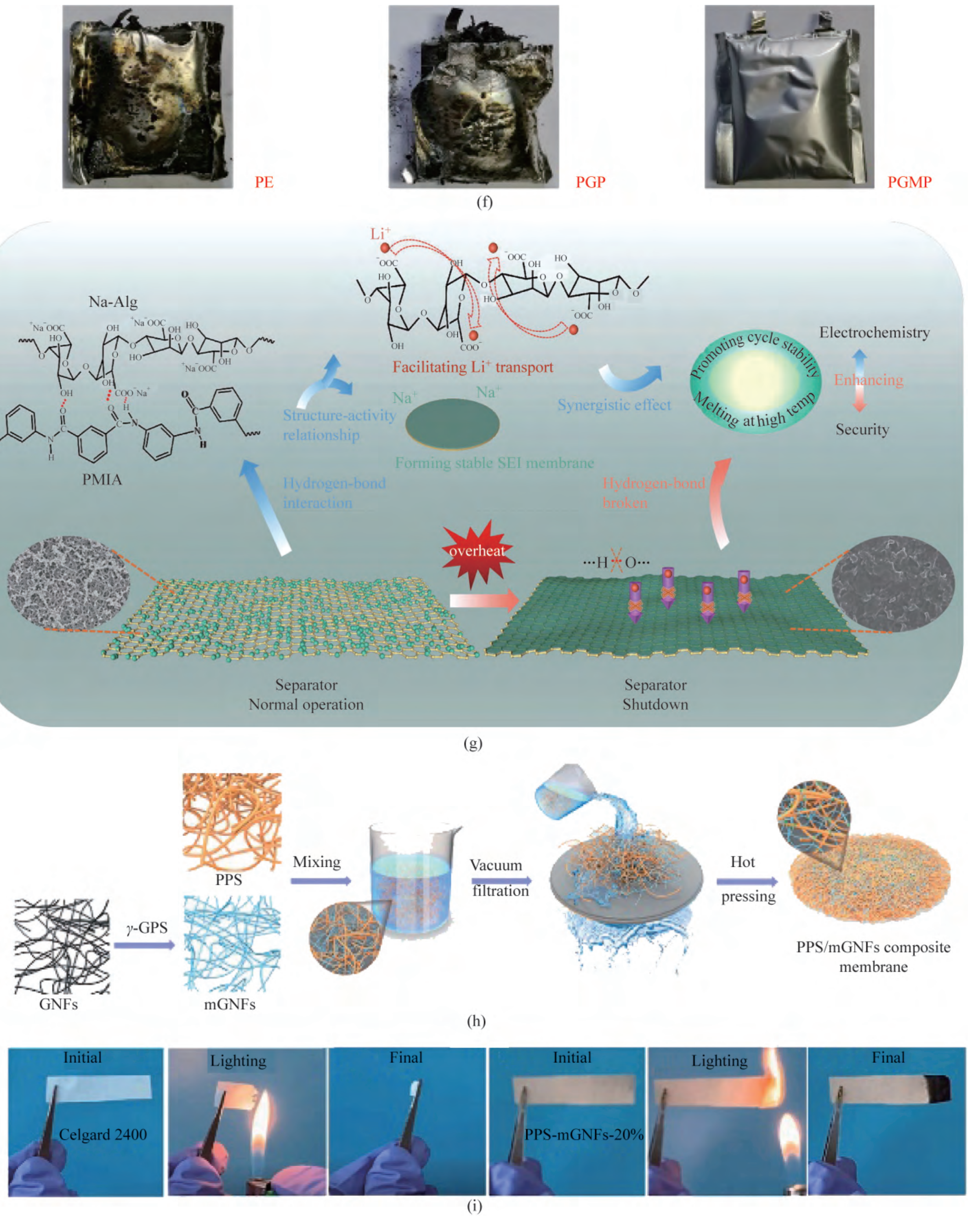


图5 (a)UiO-66@OPBI隔膜的结构示意图[82]；(b)采用ANFs隔膜和PP隔膜的电池在90℃下的循环性能；(c)采用ANFs隔膜的电池在90℃下点亮电灯泡的照片[83]；(d)PGMP隔膜的制备流程及工作机理示意图；采用PE隔膜、PGP隔膜和PGMP隔膜的电池在过充实验中的温度、电压与电流曲线(e)以及实验后的图片(f)[84]；(g)Na-Alg/PMIA隔膜的结构及工作机理示意图[85]；(h)PPS-mGNFs隔膜的制备流程图；(i)Celgard 2400隔膜和PPS-mGNFs隔膜的燃烧测试[86]

Fig.5 (a) Structure diagram of UiO-66@OPBI separator[82]; (b) Cycling performance of batteries with ANFs separator and PP separator at 90℃; (c) Photographs of a battery with ANFs separator lighting a light bulb at 90℃[83]; (d) Schematic diagram of the fabrication process and work mechanism of PGMP separator; Temperature, voltage and current curves (e) and digital images after the test (f) of batteries with PE separator, PGP separator and PGMP separator during overcharge test[84]; (g) Schematic diagram of the fabrication process and work mechanism of Na-Alg/PMIA separator[85]; (h) Fabrication process of PPS-mGNFs separator; (i) The flammability test of Celgard 2400 separator and PPS-mGNFs separator[86]

高电压下的分解和放热有关。当荷电状态达到160%时,电池电压迅速上升到10 V,温度高达300℃以上,导致电池燃烧[图5(f)]。采用PGMP隔膜的电池电压变化与使用PE隔膜或PGP隔膜的电池电压变化基本相同,但温度上升缓慢。当电池温度达到98℃时,随着充电电流的减小,电池温度逐渐降低,并且在测试后,采用PGMP隔膜的电池外观尺寸完整。另外,软包电池的钉刺和冲击等测试同样表明PGMP隔膜能够有效提升电池的安全性,且采用PGMP隔膜的软包电池热失控起始温度从120℃(采用PE隔膜的电池)提升至146℃。Chafi等[93]利用光交联工艺,在GF基体上将具有不同聚乙二醇段长度的聚乙二醇二甲基丙烯酸酯(PEGDMA)单体与Al_2O_3纳米颗粒复合,得到PEGDMA/Al_2O_3/GF复合隔膜。结果表明,PEGDMA/Al_2O_3/GF复合隔膜具有优异的电解液浸润能力,且在燃烧实验中表现出优异的阻燃性能,维持了基本的外观尺寸。聚丙烯酸酯也被引入到GF中以得到热稳定性良好的复合隔膜,并且其黏结性能可以抑制电极在工作中的膨胀和变形。

PMIA具有良好的阻燃能力和优异的热稳定性(分解温度约400℃),因此被用作隔膜材料时可显著提高电池的安全性。Hu等[85]采用非溶剂相诱导分离技术,设计并制备了具有关闭功能的热响应型海藻酸钠修饰PMIA复合隔膜(Na-Alg/PMIA)。如图5(e)所示,PMIA和Na-Alg通过氢键结合,且Na-Alg的极性基团有利于锂离子的扩散,而钠离子可以为锂离子提供活性位点,从而抑制锂枝晶的形成。结果表明,Na-Alg/PMIA隔膜在200℃下无明显热收缩,并且可以及时关闭孔隙,阻止锂离子扩散,从而将电流回路切断,防止电池内部短路。Hu等[94]利用PMIA和氟化多孔二氧化钛(F-TiO_2)之间的强氢键作用,制备了F-TiO_2/PMIA复合隔膜。研究表明,F-TiO_2/PMIA复合隔膜具有良好的机械稳定性和耐热性(250℃),且在燃烧实验中表现出优异的自熄性,大大地提高了电池的安全性。

聚苯硫醚(PPS)因具有优异的热稳定性(分解温度约450℃)、本征阻燃性以及良好的化学稳定性和绝缘性而被认为是一种很有前途的聚烯烃隔膜材料的代替品。Kim等[95]利用等离子体辅助机械化学技术改善了不相容的PPS与SiO_2混合物中SiO_2颗粒的分布均匀性,后通过刻蚀工艺制备出具有高孔隙率的多孔PPS隔膜。与PP隔膜相比,PPS隔膜表现出优异的电解液浸润性,并且具有更高的机械稳定性和热稳定性(250°C下尺寸无可见变化)。Yu等[86]利用纺丝、抽滤和热压工艺制备了一种孔隙率和孔径可控的PPS纤维/GF多孔复合隔膜(PPS-mGNFs),如图5(f)所示。热压工艺结合硅烷偶联剂(3-缩水甘油醚氧基丙基三甲氧基硅烷,γ-GPS)的改性赋予了PPS-mGNFs隔膜高的柔韧性和优异的力学性能。此外,PPS-mGNFs隔膜具有出色的热稳定性(在250℃下0.5 h无热收缩)和阻燃性能[图5(g)~(i)],保证了电池的安全性。聚氨基胺(PAMAM)枝状聚合物[96]与BC纳米纤维[97]也被研究与PPS基材相复合,以制备具有高耐热性和离子电导率的功能性隔膜。

其他具有优异热稳定性的隔膜基材,如聚芳醚腈(PEN)[98-99]、聚酰亚胺(PIA)[100]、聚醚酰亚胺(PEI)[101]、聚醚醚酮(PEEK)[102]、聚丁二酸丁二醇酯(PBS)[103-104]等被广泛研究。表4总结归纳了近年来所报道的具有高耐热性和阻燃性的其他新型隔膜的重要特性参数。通过对原材料的结构(分子结构或微观结构,如孔隙等)进行创新性设计,或与其他功能性材料进行复合,所制备出的新型隔膜均表现出比商业聚烯烃隔膜更好的耐热性和阻燃性,从而保障了电池安全且稳定的运行。

2 总结与展望

锂离子电池的能量密度与功率密度的快速提升迎合了目前人们对于电动汽车续航长、充电快的发展需求。然而,电池技术快速革新的同时,需重点关注电池自身的安全性。锂离子电池常用的聚烯烃隔膜在高温下会发生皱缩与熔化,从而加剧了电池在滥用情况下的热失控危害。相比之下,具有高热稳定性和机械强度等优异特性的新型隔膜材料能够改善电池的安全性。本文综述了锂离子电池领域中具有高热稳定性的新型隔膜,如PI基隔膜、纤维素基隔膜、PVDF-HFP基隔膜、OPBI基隔膜等的最新研究进展,并对其设计思路以及构效关系进行了讨论与总结,同时对隔膜的关键特征参数如厚度、离子电导率、热收缩率等进行了归纳与比较。

高热稳定隔膜可以在高温环境下保持结构稳定,防止电池热失控。然而,高热稳定性材料由于其结晶度较高,离子传输通道较少,往往伴随着较低的离子电导率。另外,隔膜的厚度不仅影响其机

表4　其他隔膜的物理化学特性

Table 4　Physicochemical properties of other separators

Material	Preparation method	Thickness/μm	Tensile strength/MPa	Porosity/%	Ionic conductivity/($mS\cdot cm^{-1}$)	Electrolyte uptake/%	Thermal shrinkage/%	Ref.
SCOF@Li/OPBI	casting	36	23.2	51	1.363	391	—(200℃, 1 h)	[105]
SCOF/OPBI	casting	34	8.9	58	1.76	439	0 (200℃, 1 h)	[88]
UiO-66-S-Li@OPBI	casting	31	13.5	58	1.46	249	0 (200℃, 1 h)	[106]
OPBI@COF	casting	26	15.4	60	1.214	428	—(200℃, 1 h)	[87]
UiO-66@OPBI	casting	25	10.3	63	1.74	213	—(200℃, 1 h)	[82]
GF/PPS	electrospinning, filtration and press	34	22.2	65.4	1.43	270.7	0 (250℃, 0.5 h)	[86]
PE/GF-$Mg(OH)_2$/PE	impregnation and press	65	250	61	0.93	86	—(350℃, 0.5 h)	[84]
GF/polyacrylate	impregnation and press	150	20	75.8	2.16	335	—(350℃, 0.5 h)	[107]
GF/PEGDMA/Al_2O_3	casting	50	12.7	—	—	约326	0 (458℃, —)	[93]
ANFs/CNF/diatomite/PI	filtration, impregnation and extrusion	—	23.74	69.34	1.04	237.16	0.31 (200℃, 0.67 h)	[91]
ANFs	casting	—	0.75	86.5	1.04	695	0 (300℃, 1 h)	[83]
ANFs/ZIF-8	filtration	—	52.8	61.6	1.37	224	—(200℃, —)	[90]
ANFs/PEO	electrospinning	—	41.52	75.85	4.33	650	0 (200℃, 1 h)	[92]
chitosan nanofibers	filtration	25	22	65	1.15	281	0 (160℃, 0.5 h)	[108]
polyimine aerogel	casting	50	—	78	0.92	591	0 (210℃, 0.167 h)	[100]
PPS/PAMAM/PVDF-HFP	impregnation	51	10.2	85	0.92	236	0 (200℃, 1 h)	[96]
sodium-alginate/PMIA	coating	—	—	52.5	1.26	252.3	—(250℃, 0.5 h)	[85]
fluoride TiO_2/PMIA	casting	40	24.6	73	1.3	322	—(250℃, —)	[94]
Al_2O_3/PEI	casting	30	16.2	62	1.07	165	—(350℃, /)	[101]
PBS/Mxene/SiO_2	filtration	45	约4.15	54.3	3.386	633	—(160℃, 0.25 h)	[103]
PEEK	electrospinning and extrusion	40	15.8	71.2	1.48	245.5	3.4 (300℃, —)	[102]
Alginate fiber-PEA	filtration	85	—	—	1.8	—	— (200℃, 2 h)	[109]
sulfonated cellulose/PLA/PBS	coating	35	—	87.7	3.24	290.6	0 (150℃, 0.5 h)	[104]
PEN@PDA-PEI	casting	约30	20.6	75	1.5	618	0 (200℃, —)	[98]
cellulose/PPS	filtration	60	约18	62.7	1.55	216.2	0 (200℃, 0.5 h)	[97]
$Ca_6Si_6O_{17}(OH)_2$	filtration and freeze drying	6~15	—	82	3.08	—	约2.6 (150℃, —)	[110]
PEN-IPA	casting and impregnation	30	—	73.1	1.47	400	0 (180℃, 1 h)	[99]
Li-SPEOD	electrospinning	—	6.7	65.52	3.57	476.2	0 (400℃, 0.5 h)	[111]
PPS	plasma-assisted mechanochemical treatment, compression moulding and etching	50	—	—	—	—	0 (250℃, —)	[95]
PAEK	casting	40	21.1	85	—	310	约12 (300℃, —)	[112]
sulfophenylated PEEKK/LiTFSI	electrospinning and impregnation	—	5.3	38.7	0.28	195	2 (200℃, 0.5 h)	[113]

械强度，还关系到电池的能量密度和安全性。较厚的隔膜通常具有较高的机械强度，能够更好地抵抗电池充放电过程中的形变和穿刺，但也会增加电池的内阻，降低能量密度。从材料设计的角度，实现高热稳定性、高离子电导率、低热收缩率以及合适的机械强度，需要综合考虑材料的分子结构、微观形貌以及复合方式等因素。例如，通过引入无机纳米颗粒可以显著提高隔膜的热稳定性和机械强度；通过复合高离子电导率的聚合物可以改善隔膜的离子传输性能；通过优化隔膜的孔隙结构和表面形貌可以提高其电解液浸润性。

尽管高热稳定性隔膜在提升锂离子电池安全性方面展现出巨大潜力，但其高昂的成本和复杂的制备工艺仍然是制约其商业化应用的主要因素。

从材料选择角度，利用低成本、易获取的原材料是降低隔膜成本的有效途径。例如，纤维素基隔膜以天然植物纤维为原料，不仅成本低廉，而且所得隔膜热稳定性优异。其次，开发高效的制备工艺也是降低成本的关键。例如，采用静电纺丝、溶液浇铸等低成本、易规模化的制备技术，可以显著提高隔膜的生产效率并降低制造成本。

高热稳定性隔膜的未来研究方向还可考虑以下几点：(1)继续挖掘具有更高热稳定性和机械强度的新型材料，利用先进的表征手段如原位扫描电镜、原位X射线衍射仪等对不同种类隔膜的耐高温机制进行深入探究，以从分子角度来指导新型耐高温隔膜的设计；(2)在改善隔膜热稳定性的同时，通过调控隔膜的孔径大小和分布，优化电解液的浸润性和离子的传导路径，提高隔膜的离子电导率；同时，研究隔膜孔结构对其热稳定性和机械强度的影响；(3)造成电池内部短路的锂枝晶可通过改善隔膜亲锂特性来抑制，如在隔膜制备过程中混入亲锂材料如金属氧化物、带有亲水性基团的聚合物等来实现协同提升电池安全性；(4)聚焦于耐高温隔膜对大容量软包电池热失控的抑制作用；(5)将隔膜集成于固态电解质中，以从根本上解决液态电解液易燃的问题。随着人们对于新型耐高温隔膜材料研究的不断深入，锂离子电池的安全性问题有望被进一步改善。

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