

基于多尺度结构与界面工程调控的高储能密度聚合物基电介质 复合材料

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摘 要: 电介质材料是决定电介质电容器储能特性的关键材料。聚合物基复合电介质因综合了聚合物基体和改性填料的优势已成为目前极具发展潜力的储能电介质材料。然而, 当前高度集成化和小型化的能源动力系统对电介质电容器的储能性能提出了更高的要求, 而改善性能的根本在于进一步提升聚合物基复合电介质的储能密度。本工作比较了不同种类聚合物基电介质复合材料的性能特征, 总结了其结构特点和设计思路, 从多尺度结构和界面工程调控等方面回顾了提升复合电介质储能性能的方法, 包括调控填料的微观结构、构建宏观层状结构、纳米涂覆聚合物表面、聚合物分子结构设计等策略。最后, 总结了当前聚合物基复合电介质材料面临的挑战和未来的发展趋势。

关键词: 结构设计; 界面工程; 高储能密度; 复合电介质

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为响应“十四五”规划对于提升绿色清洁能源比重和加快推动新型能源技术发展的号召, 大力推动电力储能是一种行之有效的策略。相较于电化学电容器和电池等储能技术, 电介质电容器储能具有超高功率密度、快速充放电能力、良好的循环稳定性等优势^[1-3], 在可再生能源^[4]、脉冲电力器件^[5]、微波通信^[6]等领域都有着广泛应用。但能量密度不足的问题限制了电介质电容器朝着轻量化、小型化、集成化方向发展^[7]。因此提升电容器的能量密度是适应快速发展的能源动力需求的必要措施。

本工作主要介绍了电介质的基本原理、不同类型电介质的特点以及当前电介质的主要设计思路, 并就微观结构设计、宏观结构调控 2 个角度入手, 具体从填料的微观结构、维度, 层状结构设计, 界面工程, 聚合物分子结构调控回顾了近年来聚合物基复合电介质的研究进展。另外, 除了关注常温下应用的复合电介质的储能特性还针对高温用聚合物基电介质面临的挑战和应对策略进行了梳理。最后, 对当前的聚合物基电介质存在的问题进行了总结并

对其未来的发展进行了展望。

1 聚合物基复合介电储能材料

电介质电容器是一种由电极和电介质组成的无源器件, 其中发挥关键作用的是夹在 2 块平行电极间的电介质材料^[8-9]。电介质电容器的存储与释放能量过程正是通过电介质极化和去极化实现的, 这一过程实则是束缚电荷微观位移或偶极子转向^[10]。其中主要的 4 种极化类型包括: 电子云畸变产生的电子极化、正负离子位移导致的离子极化、偶极子沿电场转动的取向极化以及多组分介质中存在的界面极化^[11-14]。充电过程, 电介质材料发生极化, 偶极子会随着外界施加的电场转向, 从而使电极板上出现感应电荷储存电能; 放电过程, 电介质去极化, 偶极子随着电场消失逐渐趋于无规取向, 储存的能量被负载利用。

电介质电容器的储存能量的过程可以通过电位移矢量-电场($D-E$)曲线直观反映。如图 1 所示, $D-E$ 曲线的斜率为电介质材料的介电常数, 反映了材料

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极化的能力大小。随着电场增加, 电介质不断被极化, 电位移不断增加, 当达到电介质所能承受的最大电场即击穿电场 E_b 时, 电位移达到最大值 $D_{\max}$ ^[10]。电容器的充电能量密度为图 1 中绿色和粉色区域。当撤去电场时, 电位移会随之降低, 但由于偶极的转向迟滞以及电介质内部的漏电流的存在, 直至电场降为 0 时仍存在一定的剩余电位移 D_r 。电位移曲线无法完全与初始极化曲线重合, 2 条曲线所包围部分即是损耗的能量 U_{loss} 。实际放电能量密度为图 1 中粉色区域。一般而言, 线性介电材料的放电能量密度可简化为式(3)^[11]。显然, 放电能量密度是 ϵ_r 和 E_b 的正相关函数, 因此提升 ϵ_r 和 E_b 是获得高能量密度电容器的关键。在实际应用中, 电容器的充放电效率 η 也是一个重要性能指标, 侧面反映了电容器的能量损耗程度^[15]。由于各种类型损耗大多是以热能形式散失, 若热量无法及时导出可能造成电介质材料热失效, 从而影响电容器的稳定运行。因此在关注高 U_d 的同时也应考虑较高的 η 。相关储能性能参数的计算公式为:

$$\text{充电能量密度: } U_c = \int_0^{D_{\max}} E dD \quad (1)$$

$$\text{放电能量密度: } U_d = \int_{D_r}^{D_{\max}} E dD \quad (2)$$

$$\text{线性电介质的放电能量密度: } U_d = \frac{1}{2} \epsilon_0 \epsilon_r E_b^2 \quad (3)$$

$$\text{充放电效率: } \eta = \frac{U_d}{U_c} \times 100\% \quad (4)$$

式中: U_c 为电容器的充电能量密度; U_d 为电容器的实际放电能量密度; E 为外加电场; D 为电位移; $D_{\max}$ 为最大电位移; D_r 为剩余电位移; ϵ_0 为电介质的真空介电常数; ϵ_r 为电介质的相对介电常数; E_b 为击穿场强; η 为充放电效率。

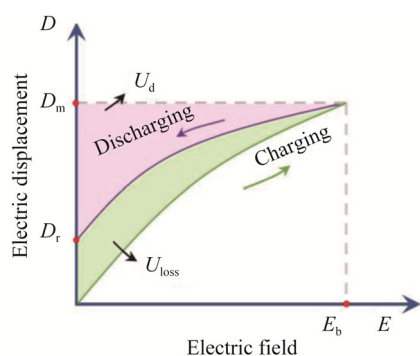


图 1 电介质材料的电位移(D)–电场强度(E)滞回曲线^[16]

Fig. 1 Electrical displacement (D)–electric field strength (E) hysteresis curve for dielectric materials^[16]

无机电介质是一类最早发现并应用的电介质^[17], 传统无机电介质可分为线性材料^[18]、顺电材料^[19]、铁电材料^[20]、弛豫型铁电材料^[21–22]、反铁电材料^[23]。而近来, 含有多种阳离子的高熵氧化物电介质凭借优异的介电性能逐渐成为研究热点^[24]。无机电介质因高的介电常数、较低的介电损耗($\tan\delta$)、优异的高温稳定性而受到广泛研究^[25]。但无机电介质中的内部缺陷限制了击穿场强的提升, 同时较大的机械强度也使得无机电介质材料难以应用于柔性电子器件^[26]。

相比于无机电介质, 聚合物电介质具有 MV/cm 量级的出色击穿场强有望应用于高电场环境以进一步提升能量密度。同时聚合物良好的可加工性, 在柔性电子器件领域有很大的用武之地^[27]。常用的聚合物电介质包括线性聚合物聚丙烯(PP)^[28–29]、聚乙烯(PE)^[30–31]、聚对苯二甲酸乙二醇酯(PET)^[32–33]以及铁电聚合物聚偏二氟乙烯 PVDF 及其共聚物聚偏氟乙烯–六氟丙烯 P(VDF–HFP)^[34–35]等。但大多数聚合物都有介电常数低(<10)的问题, 因此其储能特性表现为较低水平^[36–38], 例如常见的商用线性聚合物双向拉伸聚丙烯(BOPP)常温下的介电常数仅为 2.2, 能量密度也仅有 2~3 J/cm³^[39]。基于此, 研究人员开始将目光投向聚合物基复合电介质, 以期同时结合改性填料与聚合物基体的各自特长, 进一步提升电介质材料的能量密度。

研究人员尝试将高介电常数的无机填料例如二氧化钛 TiO_2 (TO, $\epsilon_r=100$ ^[40])、钛酸钡 BaTiO_3 (BTO, $\epsilon_r \approx 5\,000$ ^[41–43])、钛酸锶钡 $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$ ($\epsilon_r \approx 4\,655$, 100 MHz^[44])、锆钛酸铅 $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ($\epsilon_r > 10^3$, <40 Hz^[45])、钛酸铜钙 $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCCTO, $\epsilon_r \approx 10^4$, 100 kHz^[46–47])等加入聚合物基体以获得高介电常数的复合电介质。然而, 介电常数的提高往往需要高填充量的无机填料, 但大量纳米填料易在比表面能的驱动下发生团聚, 以及无机填料与聚合物间过大的极化性能差异, 同时加剧了局部的电场集中进而损害复合材料的击穿场强。为了缓解纳米填料的团聚问题, 研究者已经开发出化学处理、热处理、等离子体处理等多种表面改性手段来改善填料与聚合物基体的相容性。其中化学处理即使用化学试剂在纳米填料表面修饰官能团, 从而降低纳米填料的表面能, 增强填料与聚合物基体的界面结合。例如使用过氧化氢使纳米填料表面羟基化^[48], 极性的羟基不仅能增强纳米填料的取向极化, 也能促进电荷散射。同时在纳米填料和聚合物基体间形成的氢键也

增加了两者的界面键合,有利于提升复合电介质的击穿性能。纳米金属氧化物填料表面硅烷化处理也是促进填料均匀分散以改善电介质介电性能的有效手段。Huang 等^[49]将多面体低聚倍半硅氧烷(POSS)功能化氮化硼纳米管 BNNTs 掺杂进入环氧树脂中,制备出了具有高导热和低介电损耗的环氧纳米复合电介质。Khodaparast 等^[50]利用硅烷偶联剂改性制备的 TiO_2 实现了在 PVDF 基体中的均匀分散,有效提升该复合电介质的介电常数。Niu 等^[51]采用天青石蓝修饰 BTO 表面,促进 BTO 填料在 PEI 基体中均匀分散,含有 2% (体积分数)修饰后 BTO 的 PEI 薄膜的能量密度是 2%无修饰的 BTO/PEI 复合薄膜的 3 倍。虽然表面改性能够实现纳米填料在聚合物基体中的均匀分散,但无法解决两者的过大介电常数差引起的电场畸变问题。对无机纳米填料的结构设计有望弥合无机填料与聚合物基体间过大的极化特性差异。在对填料微观改性的基础上,复合电介质的宏观结构设计也被提出,三明治结构甚至数十层的叠层状结构策略相继出现。

由能量密度[式(3)]可知,击穿场强相对于介电常数对于材料能量密度的影响更为突出,获得高能量密度对复合材料击穿场强提出了更高的要求。大量研究表明聚合物基复合电介质的击穿行为是一系列因素综合作用的结果,其中填料的尺寸、填料的介电性能、填料含量是 3 个较为重要的因素^[52–55]。Yue 等^[56]采用高通量随机击穿模拟和机器学习研究这 3 个因素对于复合电介质击穿行为的影响。具体而言,该研究采用单一变量法研究各因素对于 E_b 的影响,结果发现:1) 填料的尺寸越大,电树会呈现更加曲折的发展,意味着电树延展过程的阻碍变大, E_b 增大。即维度更高、尺寸越大的填料将会呈现更优异的电树阻挡效应,能够有效提高聚合物基复合电介质的 E_b ^[57]。2) 填料的含量也会显著影响 E_b ,当填料过少时,填料对于电树的阻碍作用很弱,而当填料过多时,填料团聚几率增大,填料团聚会引发局部电场畸变,诱导电树更快扩展,导致 E_b 降低。因此选择合适的填料含量也是提升 E_b 的关键。3) 填料的高介电常数与聚合物的低介电常数的失调会导致电场分配不均,诱导快速击穿路径的形成。因此一系列调控梯度介电常数的策略被开发出来,例如设计核壳状的填料以形成不同介电常数数值之间的良好过渡、宏观层状结构调节电场的分布等^[58]。

高压下电介质的电树击穿问题始终是影响介电

材料绝缘性能的干扰因素。为了保持电介质电容器稳定运行并延长其使用寿命,提升电介质材料在高场、高温下的自我修复能力是可行的策略。有研究人员发现在热塑性聚合物中添加微量磁性纳米颗粒能够修复聚合物基体中电击穿破坏区域,其作用机制为磁性纳米颗粒在振荡磁场作用下迁移到聚合物电击穿部位并放出热量,促使热塑性聚合物熔融后重新修复,实现电树损伤部位的自愈合。Yang 等^[59]使用聚乙二醇对超顺磁性氧化铁纳米颗粒进行表面改性,添加小于 0.1% (体积分数)的表面功能化磁性粒子的商用聚丙烯(PP)表现出对电树击穿优异的愈合能力。在此基础上,Gao 等^[60]探索了热固性塑料的自愈合方法,其利用电树过程的电致发光触发微胶囊释放出愈合剂并发生愈合剂的交联,从而填充电介质的受损区域。除此之外,基于阴离子聚合的微胶囊法^[61]、微波磁场双响应微球与热固性聚合物的交联复合材料在外磁场下的靶向修复^[62]也是目前具有前景的自愈方法。自愈合聚合物基电介质的开发为推动电介质电容器在高压极端环境中发挥储能优势提供了坚实保障。

为适应当前电动汽车、航空航天领域高温的应用场景,具有高温稳定性和高玻璃化转变温度($T_g > 150\text{ }^\circ\text{C}$)聚合物如苯并环丁烯(BCB)^[63]、聚酰亚胺(PI)^[64–65]、聚醚酰亚胺(PEI)^[66]、茆聚酯(FPE)^[67]、聚醚醚酮(PEEK)^[68]、聚碳酸酯(PC)^[69–70]等已经引起了研究人员的关注,这些高温聚合物中的芳香结构或稠环杂环结构赋予其优异的高温稳定性^[71]。但高温聚合物电介质在高电场和高于 T_g 的高温下工作时,聚合物会发生微布朗运动,促进载流子迁移,造成电导损耗的显著提升和击穿电场的大幅下降,严重恶化了电介质的介电性能。例如,150 $^\circ\text{C}$ 时 PEN、PI、PC 的 U_d 均不足 0.3 J/cm^3 ^[72]。

在高温恶劣条件下,能够正常工作的电容器要求电介质材料在保证介电性能的同时也保持一定的热稳定性和机械强度。因此聚合物电介质在高温应用时需要解决的问题主要有:1) 聚合物电介质在高温下显著的电导损耗可能造成热击穿等不良影响,因此要求聚合物电介质具备一定的内部散热能力。但聚合物的热导率普遍 $< 0.5\text{ W/(m}\cdot\text{K)}$ ^[73]。针对此问题,目前常用的策略包括添加高导热填料、聚合物基体表面涂覆处理、聚合物基体中构建导热骨架等。例如 Guo 等^[74]研究尝试将经过表面功能化处理的氮化硼(f-BN)添加到 PI 中,30% (质量分数)f-BN/PI 复合电介质的热导率从纯 PI 的 $0.21\text{ W/(m}\cdot\text{K)}$ 提升至

0.71 W/(m·K)。2) 当聚合物电介质在接近 T_g 工作时, 其机械完整性和介电性能会显著恶化, 特别是高于 T_g 工作时, 随着温度升高, 聚合物分子链的链段运动加剧, 机械强度下降, 漏电流和介电损耗也大幅增加。针对上述问题, 近年来研究主要是采取聚合物表面进行纳米涂覆以形成界面高能垒阻碍电极电荷注入和聚合物内部引入深陷阱捕获移动电荷 2 种策略。

2 聚合物基复合介电储能材料的研究进展

2.1 含有核壳/同轴结构填料的复合电介质

聚合物基复合材料往往采用高介电常数填料掺入聚合物基体中, 以增强复合材料整体的极化作用。例如 Ou 等^[75]使用熔盐辅助法制备了缺铜结构的钛酸铜钙 $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO), 64% (体积分数) 改性 CCTO 掺杂的 PVDF 基复合电介质的介电常数从纯 PVDF 的约 12 提升至 939。但填料与聚合物基体间的介电常数差异过大引发填料周围电场集中, 从而产生局部较大的电应力, 成为电树的发展起点, 反而削弱了复合电介质的击穿场强和储能表现^[76]。近期不少研究致力于纳米填料的微观调控以改善电场集中问题, 其中典型的方法为纳米填料与聚合物之间引入介电常数中等的过渡层。利用这一思路构建的核壳结构纳米填料已经得到广泛研究^[77]。Ren 等^[78]将宽带隙 Al_2O_3 作为外壳包覆在 ZrO_2 表面构筑了全无机核壳结构填料分散于高温聚合物 PEI 基体中。该无机核壳结构不仅能够形成有效的介电常数梯度以缓解电场局部的畸变, 而且宽带隙的外壳形成的深陷阱能够有效抑制漏导从而大大提升复合电介质的击穿场强。此外, 无机填料还具备有机壳层

所欠缺的高温稳定性从而能拓宽复合电介质的应用温度范围。结果表明, 150 °C 时, 含有 11% (体积分数) $\text{Al}_2\text{O}_3@\text{ZrO}_2$ 的 PEI 纳米复合材料的击穿场强较纯 PEI 提升 33.3% (585 MV/m v.s. 439 MV/m), 并保持 $\tan\delta \approx 0.004$ 的低介电损耗。除了全无机结构, 也有研究将有机物作为外层壳, 以改善无机填料与聚合物的界面接触。例如 Jiang 等^[79]以耐热聚合物聚对苯撑苯并二噁唑(PBO)为基体, 通过可逆加成-断裂链转移聚合在高导热性 CCTO 纳米颗粒表面包覆上一层与 PBO 结构类似的聚(2-异丙基苯并噁唑)(P(2-IBO))外壳, 从而促进 CCTO 与 PBO 间的界面相容性, 进一步优化了介电性能(图 2)。修饰后的 CCTO/PBO 复合电介质的击穿场强较未修饰的 CCTO/PBO 大幅提升, 且在 200 MV/m 下的 U_d (3 J/cm³) 是纯 PBO 的 50 倍。有研究显示, 更大纵横比的一维纳米纤维比零维纳米颗粒对复合电介质的介电性能提升更显著^[80]。Zhang 等^[81]将 BTO 纳米颗粒嵌入 TO 纳米纤维中制备了 BTO@TO 复合纳米纤维, 并掺入 P(VDF-HFP) 基体中形成纳米复合薄膜。一维大纵横比纳米纤维相比于零维纳米颗粒能够增加电子散射并使击穿电树发生弯曲, 从而削弱电击穿过程造成的不利影响, 同时引入的内部界面也极大提升了复合薄膜的界面极化。含有 3% (体积分数) BTO@TO 的复合薄膜具有优异的击穿场强 ($E_b \approx 797.7$ MV/m) 和超高的能量密度 ($U_d \approx 31.2$ J/cm³)。Chen 等^[82]采用原位聚合法制备了一维同轴结构的聚吡咯包裹的海泡石纳米纤维(PPy@Sep 纳米纤维), 由于 PPy 与 PVDF 间优异的相容性, 纳米纤维均匀分散在 PVDF 基体中, 实现了介电常数的大幅提升: 100 Hz 下 5% (质量分数) PPy@Sep/PVDF 的 ϵ_r 可从纯 PVDF 的 12 提升至 40。

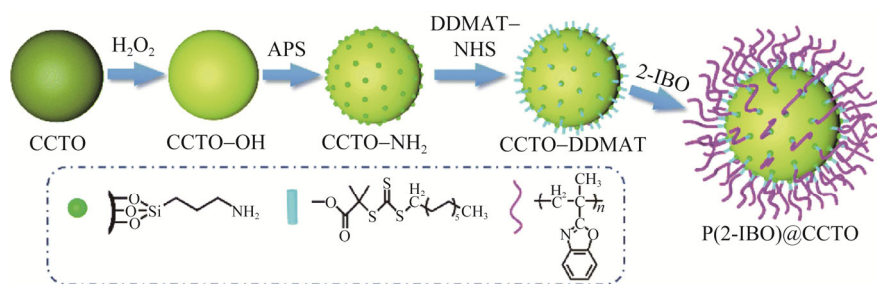


图 2 核壳结构 P(2-IBO)@CCTO 纳米颗粒的合成^[79]

Fig. 2 Synthesis of core-shell structured P(2-IBO)@ $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) nanoparticles^[79]

2.2 含有二维填料的复合电介质材料

在聚合物基体中添加零维/一维纳米填料已经被证明是一种提升复合电介质的综合介电性能的有效方法^[83-84]。但纳米填料较大的比表面积导致的颗粒团聚始终是一个棘手的问题。尽管通过填料表面改性^[51, 85-87]、表面包覆^[88]、原位聚合^[89]等方法能够

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改善这一情况,但工艺过程太过繁复、效益不高。近年,二维填料也被引入聚合物基体中,其显示出许多独特优势:1) 二维填料大的纵横比增大了内部偶极矩,赋予其更优异的极化性能;2) 二维填料相较于零维/一维填料具有更小的比表面积和表面能,因此与基体的相容性更优异,易实现在聚合物基体中的良好分散,从而获得更致密的复合结构和更少的结构缺陷;3) 二维填料分散在聚合物基体中可以作为天然的物理屏障,增大载流子的散射,延缓电击穿的发生。Li 等^[90]尝试二维填料和零维纳米填料共同作用提升聚合物电介质的介电性能,其中二维填料阻碍电树延展和纳米填料聚集,零维填料提升介电常数,实现了高 ϵ_r 与高 E_b 并存。聚合物在高温下的高电导损耗是聚合物高温介电性能恶化的主要原因,高的电导损耗不仅限制了能量密度还造成了低电场下的击穿行为,同时高

损耗引发的热失控也威胁器件安全运行^[71]。在高温聚合物基体中加入宽带隙无机填料是降低电导损耗的常用方法。Li 等^[91]将具有高导热、宽带隙的氮化硼纳米片(BNNSs)添加进交联的 BCB 获得 c-BCB/BNNSs 纳米复合材料,在 200 °C 和 200 MV/m 的条件下其高温电导率相较于 c-BCB 降低了 2 个数量级,仅为 9.2×10^{-14} S/m。如图 3 所示,随后该团队又尝试将比 BNNSs 具有更大带隙和 ϵ_r 值的 γ - Al_2O_3 制成纳米颗粒(NPs)、纳米线(NWs)和纳米片(NPLs)与交联的 BCB 进行复合。所制备的含有 7.5% (体积分数) Al_2O_3 NPLs 的复合电介质具有优异的高温介电表现,在 200 °C 的 E_b 能达到 482 MV/m,高于先前制备的 c-BCB/BNNSs($E_b=416$ MV/m)。这可以归因于纳米片对于电树生长的较大阻力以及在基体中平行分布的纳米片对外电场的良好分散避免了局部电场集中。

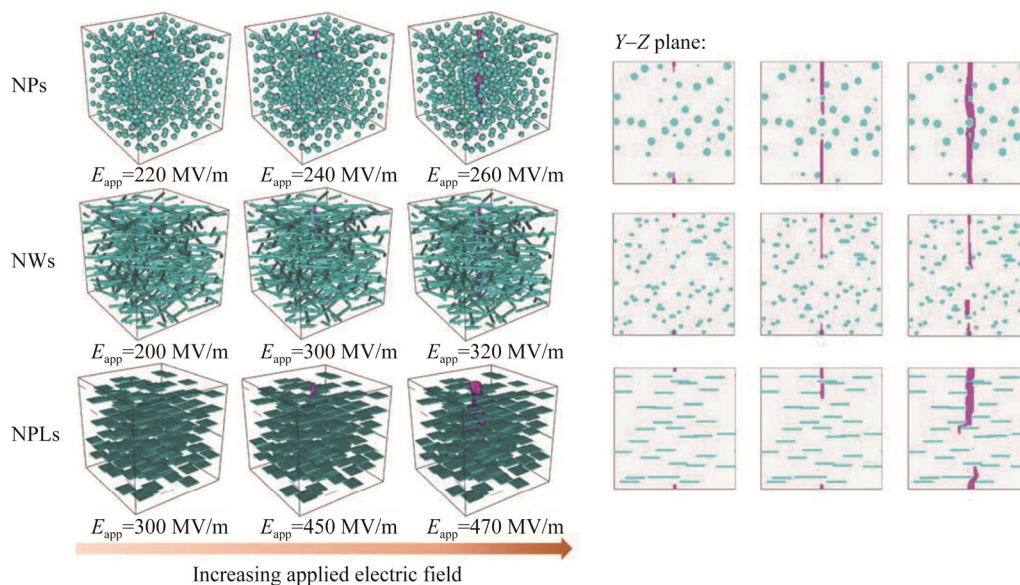


图3 7.5% (体积分数) Al_2O_3 NPs、NWs 和 NPLs 组成的 c-BCB 纳米复合材料的预测击穿路径^[91]

Fig. 3 Predicted breakdown path evolution of the c-benzocyclobutene (c-BCB) nanocomposites with 7.5% (in volume fraction) Al_2O_3 nanoparticles (NPs), nanowires (NWs), and nanoplates (NPLs)^[91]

2.3 层状结构复合电介质

在单层复合电介质结构中,往往需要添加大量(>30%, 体积分数)纳米填料以提升复合电介质的介电常数,然而这势必影响复合电介质的击穿表现。根据渗流理论^[92–93],聚合物基复合电介质存在渗流阈值,当填料的添加量超过渗流阈值时会导致填料之间相互连接,增大漏电流,而且还可能导致纳米填料局部富集和局部空缺,引起电场畸变,削弱击穿场强。对于单层复合电介质,兼具高 E_b 和 ϵ_r 仍是一个挑战。为了调和这一矛盾,复合电介质的宏观层状结构设计被提出。一种思路是通过控制不同层

的填料含量来改变介电常数,调控外加电场在复合电介质中的分布,利用高填料含量层实现高介电常数,而低填料含量层形成局部弱电场抑制电树发展过程,从而同时赋予复合电介质高 ϵ_r 和高 E_b 。另一种思路是基于材料和工艺设计全有机层状结构,热固性聚合物表面发生膨胀效应引起界面处独特的分子堆积结构,形成界面深陷阱区捕获空间电荷,实现远低于纯聚合物膜的体积电导率,同时层状膜的击穿场强和介电常数均优于纯聚合物膜。

Wang 等^[94]设计了软层/硬层/软层的三明治结构复合材料,通过调节层中 BTO 含量分布实现抑制

电树生长。其中(10%~50%, 体积分数)BTO/PVDF 层作为软层提升复合材料的介电极化, 1%(体积分数) BTO/PVDF 作为中间硬层以提升击穿场强。有限元模拟结果显示, 电树生长在层间交界处受到抑制(图 4)。其中软层含有 20% (体积分数) BTO 时的三明治结构复合材料具有 470 MV/m 的击穿强度以及 18.8 J/cm^3 的能量密度。为改进聚合物的高温储能应用, 近年来针对高温电介质的层状结构设计也不断涌现。Zhang 等^[95]通过调节滚筒转速控制静电纺丝纳米纤维取向排列, 再利用热压技术和淬火处理得到 10 层 BTO/P(VDF-HFP)致密薄膜(图 5)。其中, BTO 纳米纤维在相邻层中正交排列的纳米复合材料在三维方向上的击穿路径均变宽, 测试结果显示该结构有效增加外加电场击穿的能垒, 显著降低了漏电流。此外, 层状膜的击穿场强和介电性能

均有效提升(691.9 MV/m v.s. 644.1 MV/m ; 在 1 kHz 时 17 v.s. 8), 在 690 MV/m 下表现出 25.5 J/cm^3 的优异放电能量密度。由此可见, 层状结构的单层可调性给予了复合电介质实现不同功能化的极大空间, 为实现电介质介电常数与击穿强度的解耦提供可能。Niu 等^[96]设计了三明治结构 PEIs-PI-PEIs 全聚合物高温介电聚合物薄膜, 由于热固性聚合物 PI 表面在接触 PEIs 溶液后发生膨胀作用从而在异质界面处形成新的分子排列结构, 该结构使得层状膜在界面处形成深阱能级从而促进空间电荷在界面处发生积累, 大大减小了层状膜的高温电导率, 优化了高温介电性能。结果显示, 150°C 和 250 MV/m 层状膜的能量损耗为 0.06 J/cm^3 , 仅为纯 PI 膜能量损耗的 2.9%, 且 200°C 时保持充放电效率大于 90% 的 U_d 可达 2.0 J/cm^3 。

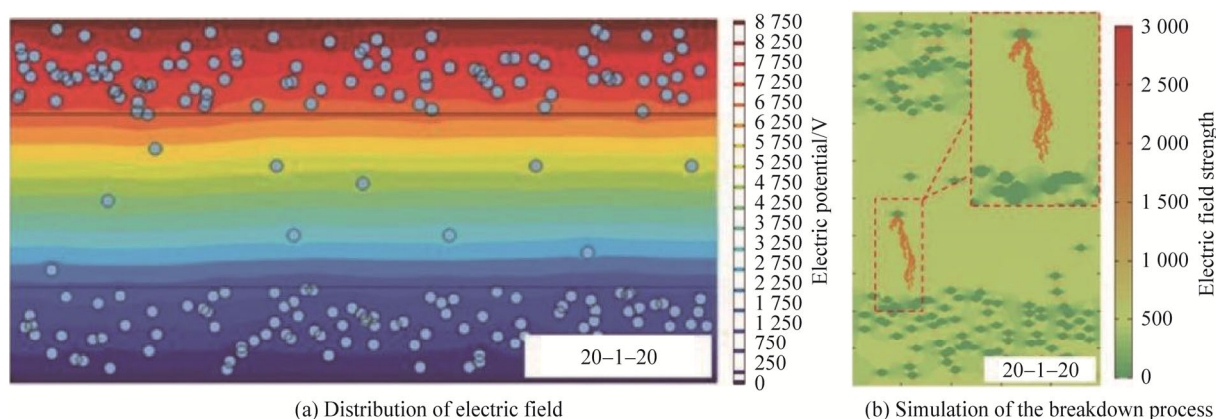


图 4 三明治结构 BTO/PVDF 纳米复合材料[“20-1-20”, “软层”含有 20% (体积分数)BTO、“硬层”含有 1% (体积分数)BTO]的电场模拟^[94]

Fig. 4 Electric field simulation of sandwich BaTiO_3 (BTO)/polyvinylidene difluoride (PVDF) nanocomposites (“20-1-20”, with 20% (in volume fraction) BTO in “soft layers” and 1% (in volume fraction) in “hard layer”)^[94]

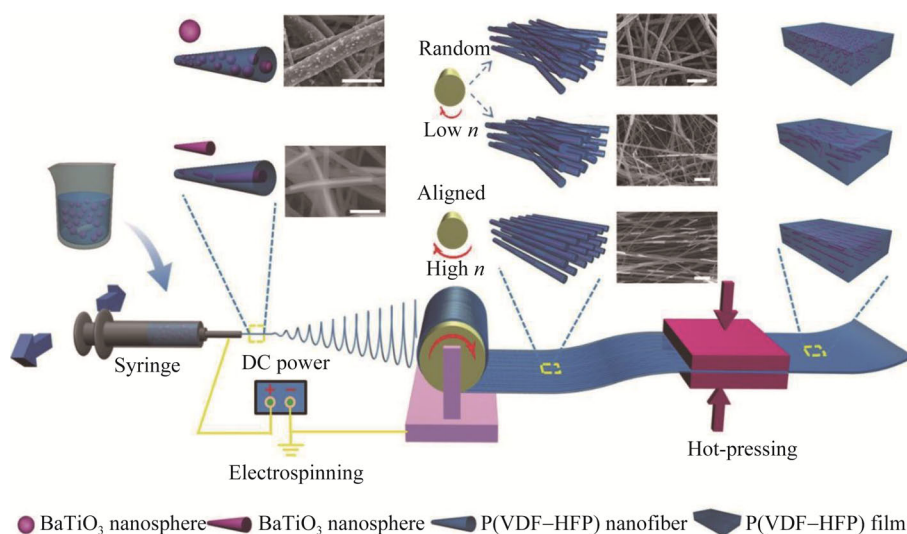


图 5 非平衡工艺制备 P(VDF-HFP)/ BaTiO_3 纳米复合纳米材料示意图^[95]

Fig. 5 Schematic illustration of non-equilibrium methods fabricating P(VDF-HFP)/ BaTiO_3 nanocomposites^[95]

聚合物复合材料宏观层状结构设计在实现高能量密度方面已经被广泛证明是有效的方法^[97–100], 但 U_d 的提高也往往伴随着 η 的下降, 实现 U_d 和 η 的兼得仍具有挑战。将线性电介质和非线性电介质结合有望破解这一难题。其中线性介电层提供高 E_b 和 η , 非线性介电层提供高 U_d 。Chen 等^[101]以聚甲基丙烯酸甲酯(PMMA)为线性中间介电层, 以含有丙烯酸橡胶的非线性 P(VDF-HFP)为非线性两侧介电层, 制备的三层复合薄膜在 11.8 J/cm^3 的高 U_d 下仍具有 89% 的高效率。

以往的三明治结构和多层结构通常是对称的, Sun 等^[102]首次尝试将目光转向非对称层状结构, 随后不对称层状结构开始受到关注^[103]。这种非对称结构主要是在线性介电层和非线性介电层中间加入过渡层以均匀电场、改善电场畸变。这一策略为实现改善 η 和 U_d 的制约关系提供了新的思路。

2.4 纳米涂层修饰聚合物

根据 Schottky 模型, 高温时电极电荷受热激发越过电极与电介质界面处势垒, 造成大量电荷迁移至电介质中引发电导损耗。因此降低高温下电导损耗的另一种策略是在聚合物薄膜表面覆盖宽带隙无机涂层, 以增加电极与介质界面处的势垒, 抑制来

自电极的电荷注入^[104]。Dong 等^[105]在含有核壳结构 BTO@SiO₂ 的 PI 基复合电介质薄膜表面原位涂覆宽带隙的 Al₂O₃ 涂层从而实现了纳米复合材料击穿强度和高温储能性能的双重提升。Zhou 等^[72]采用放电等离子增强化学气相沉积(PECVD)实现了室温和大气压下的宽带隙($\approx 9 \text{ eV}$)二氧化硅双面均匀沉积的 BOPP 薄膜。该方法表明表面沉积层能够抑制电荷注入, 有效提升复合薄膜高温下的电阻率和储能密度(图 6)。120 °C 下, BOPP-SiO₂ 薄膜的充放电效率 η 仍 $> 90\%$, U_d 为 1.33 J/cm^3 。此外该工作还尝试了将 PECVD 技术推广应用于其他高温聚合物电介质材料, 经过 SiO₂ 表面修饰的 PEI, PI, PC 的电容性能都得到大幅提升。尽管表层涂覆能有效抑制电荷注入, 但仍存在少量穿透电荷导致一定程度的漏导电流。此外气相沉积法复杂的工艺流程和较高的成本也不利于规模化生产。因此迫切需要一种便捷、高通量的制备方法与复合材料结构设计解决上述问题。Dong 等^[106]采用快速、低成本的溶液浇筑法制备了介电聚合物与宽带隙的无机氧化层的叠层复合电介质。叠层结构设计不仅抑制电荷注入同时在内部也引入深陷阱以阻碍载流子的运输。具有该结构的 Al₂O₃-PI-Al₂O₃-PI-Al₂O₃ 复合膜表现出优异的

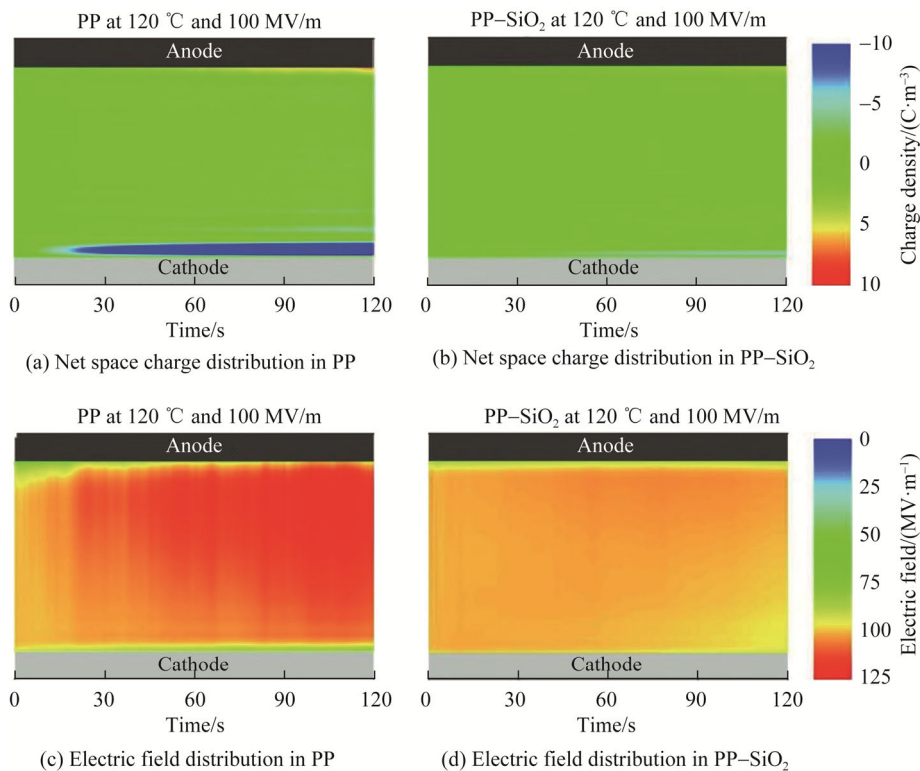


图 6 PP 和 PP-SiO₂ 薄膜在 120 °C 和 100 MV/m 条件下脉冲电声法测量的净空间电荷分布和电场畸变^[72]

Fig. 6 Net space charge distribution and electric field distortion in pristine polypropylene (PP) and PP-SiO₂ films measured by the pulsed electroacoustic method at 120 °C and 100 MV/m^[72]

高温介电性, 200 °C 的 U_d 从纯 PI 的 0.24 J/cm^3 提升至 1.59 J/cm^3 , 且在 200 MV/m 和 150 °C 的漏导电流仅为 $2.84 \times 10^{-9} \text{ A/cm}^2$ 。Wang 等^[107]设计了二维蒙脱土片(MMT)涂层修饰在 BTO/PAI 层状纳米复合材料(LN)外表面(outsideM-LN)、内部层状界面

(insideM-LN)以及内外界面(bothM-LN)的 3 种复合电介质薄膜, 利用表面涂层阻碍电荷注入和内部涂层耗散穿透电荷相结合的方式有效降低了电导损耗(图 7)。该复合薄膜在 200 °C 下的放电能量密度可达 2.48 J/cm^3 , 较无界面涂层结构提升了 536%。

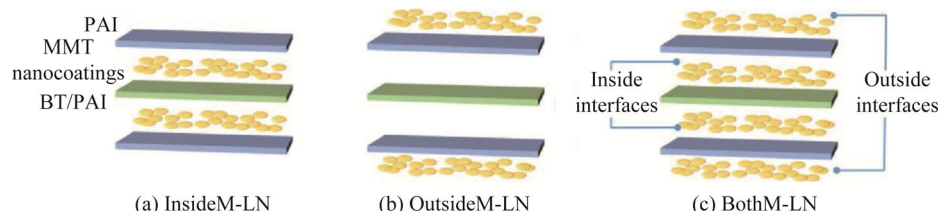


图 7 蒙脱土片涂层修饰的 3 种 BTO/PAI 层状纳米复合材料示意图^[107]

Fig. 7 Schematic illustrations of three kinds of montmorillonite (MMT) nanocoating modified BTO/PAI layered nanocomposites^[107]

2.5 分子工程

2020 年, Wang 团队首次提出对介电聚合物分子链进行接枝或者交联处理, 引入电荷捕获位点, 阻碍电荷运输, 从而提升聚合物基复合电介质的高温介电性能^[108]。随后许多研究人员应用该分子工程改性高温聚合物分子的思路研发出了一系列高温储能性能优异的复合电介质材料^[109]。如图 8 所示, Pan 等^[110]尝试通过全有机聚合物交联捕获电荷, 采用非晶聚(苯乙烯-共马来酸酐)(SMA)与 3 种不同的交联剂乙二醇(EG)、4-氨基苄醇(AA)和 4, 4'-二氨基二苯醚(ODA)共混, 使得 SMA 的主链通过柔性酯基或刚性亚胺基相连接形成交联网络。3 种交联聚合物中刚性越强的交联结构呈现出更深的能量陷阱、更高的热稳定性从而表现出更优异的击穿强度。Dong 等^[111]将宽带隙氨基多面体低聚倍半硅氧烷(NH_2 -POSS)连接到 PI 的链段, 诱导 PI 端部形成深阱, 杂化膜展示出远优于聚合物纳米复合材料的高温介电储能特性(图 9), 其中 NH_2 -POSS 含量为 3% (质量分数)的 PI 杂化膜(PI-3.0)在 200 °C 的 $U_d=3.45 \text{ J/cm}^3$, 并且能够稳定循环 $>5 \times 10^4$ 次。Chen 等^[112]合成了聚[*n*-4-氨基苯基硫酰基-双(降冰片烯吡咯烷)](PSBNP)与高电子亲和性聚(*n*-4-氨基苯基三氟乙基-降冰片烯亚胺)(PTNI)的梯状共聚物 PSBNP-co-PTNI。其中含有 2% (摩尔分数)PTNI 的 PSBNP-co-PTNI_{0.02} 在

高温高场下的电导率远远小于现有最优异的高温聚合物电介质 PEI。此外, 该共聚物还表现出卓越的高温介电性能, 200 °C 仍具有 730 MV/m 的超高击穿强度, 已经接近 BOPP 在常温的最高击穿强度, 并且具有极低的损耗(<0.007)和优异的储能特性(5.34 J/cm^3)。能带测量结果揭示了梯状共聚物具有优异高温电容性的原因, PTNI 的最高占据分子轨道(HOMO)能级(4.03 eV)略低于 PSBNP(3.14 eV), 因此在交替连接的梯状共聚物中间形成了捕获电荷的深陷阱, 从而有效抑制共聚物在高温时的电导损耗。密度泛函理论(DFT)模拟结果显示 SBNP-TNI-SBNP 单元具有比 SBNP-SBNP-SBNP 单元更低的电子跃迁能, 证明梯形结构能够有效捕获载流子。特别的是, 得益于梯形共聚物高度有序的阵列结构和强 π - π 层间相互作用, PSBNP-co-PTNI_{0.02} 展现出 $(1.96 \pm 0.06) \text{ W/(m} \cdot \text{K)}$ 的优异通平面导热系数。以往引入陷阱的方式通常是设计聚合物分子链结构或改进聚合物基体中宽带隙填料的分布, 然而这些方式往往只能产生较小的陷阱能级。Yuan 等^[113]尝试了将具有电子亲和力的分子半导体与聚合物混合制备全有机复合电介质, 其中分子半导体通过静电吸引来形成更深的陷阱能级。该设计的独特之处在于热稳定的分子半导体即使高温高场下也能够有效固定载流子, 从而为拓宽复合电介质最高的应用温度提供了更多可能。

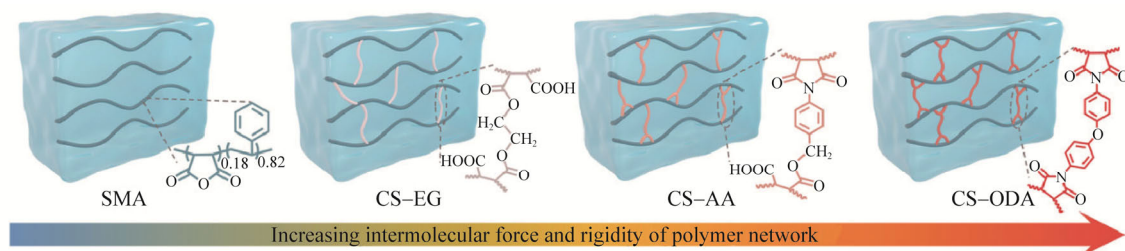
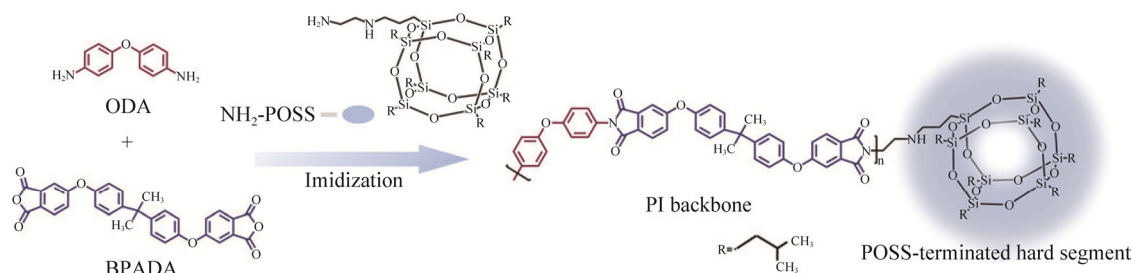


图 8 SMA 和交联聚合物的结构^[110]

Fig. 8 Structures of styrene maleic anhydride (SMA) and the crosslinked polymers^[110]

图9 原位制备PI链端系有机硅酸盐杂化膜示意图^[111]Fig. 9 Schematic illustrations of the *in-situ* fabrication of polyimide (PI) chain-end tethered organosilicate hybrid films^[111]

3 总结与展望

当前, 研究人员对优化聚合物基电介质的储能密度进行了一系列卓有成效的工作, 小至填料和聚合物分子链的微观结构设计, 大至复合电介质的界面和宏观功能化结构调控, 针对常温应用的复合电介质的介电储能性能提升和高温应用时的电导损耗问题提出了众多的解决方案。然而, 仍有一些问题有待进一步明确和改进:

1) 尽管有许多研究已经尝试核壳结构/同轴结构甚至二维填料掺入聚合物基体中并有效提升复合电介质的介电常数和击穿场强, 但鲜有研究针对于填料与聚合物基体间的界面作用机制, 以及填料在聚合物基体中的分散和取向控制等问题进行讨论。针对这一问题进行突破, 有望促进聚合物与填料之间的协调作用, 以进一步发挥出复合电介质的储能潜力。

2) 三明治结构以及多层结构设计已经被证明能够有效调控电场分布, 抑制电树枝发展, 然而对于异质界面的相容性以及层状结构的极化行为以及击穿机制的研究还有所欠缺。

3) 目前的聚合物基电介质复合材料的制备方法通常都是低通量、小规模化的实验室手段, 距离实际应用还要很长距离, 目前亟需开发低成本、高通量的生产工艺以适应大批量工业生产。

4) 为缓解聚合物基复合电介质材料高温下发生电导损耗而引发热量聚集问题, 常用的手段是在聚合物中添加高导热填料, 然而除了金刚石和BN等物质外, 大多数绝缘性能优异的填料普遍展现出不佳的导热性, 如何实现导热性与绝缘性的平衡是一个待研究的课题。

5) 建立界面屏障和内部引入深阱是目前高温聚合物基复合电介质降低电导损耗的常用手段, 这2种方法的共性都是通过抑制载流子运输起作用的, 除此之外, 针对不可避免的少量的载流子的耗

散的研究也将是一个待发掘的重要方向, 有望与前者方式结合实现“双管齐下”降低电介质的高温损耗。

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High-Energy-Density Dielectric Polymer Composites Based on Multiscale Structure Design and Interface Engineering

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Extended Abstract

Among various types of energy storage devices, dielectric capacitors show unique advantages such as a high power density and a fast charge/discharge rate. The dielectric material is a key material that affects the energy density of dielectric capacitors. Dielectric capacitors complete the storage and release of energy precisely through the polarization behavior of the dielectrics. To achieve a goal of dielectric capacitors to gradually move towards lightweight, small-sized, and integration, it is necessary to further improve their energy density. Dielectric constant and breakdown field strength are two important factors affecting the energy density of dielectrics. However, improving the dielectric constant and breakdown field strength is still a great challenge.

As different types of dielectrics are thoroughly investigated, polymer-based composite dielectrics show a great potential for energy storage because they have a high dielectric constant and a low dielectric loss of inorganic dielectrics, and a unique flexibility and a superior breakdown resistance of polymers. However, there are some problems with polymer-based composite dielectrics that restrict the further improvement of their energy density. It is necessary for the improvement of the dielectric constant of polymer-based composite dielectrics to add a high content of dielectric constant fillers. However, a high content of fillers is prone to agglomeration. Large polarization differences between fillers and polymer matrix result in an interfacial compatibility issue, leading to an early breakdown in composite dielectrics. It is thus difficult to effectively improve the energy density.

The structural design of the fillers and the macrostructural modulation of the dielectric composites are expected to optimize the dielectric properties. The core-shell/coaxial structure of fillers can be designed to alleviate the problem of decreasing breakdown field strength due to the large difference in dielectric properties between polymers and fillers. For instance, cladding the filler surface with a material of medium dielectric constant can improve the electric field distortion. Recent studies reported the introduction of two-dimensional fillers with large aspect ratios into polymer matrices. Two-dimensional fillers have a smaller specific surface energy, which makes it easy to achieve a uniform dispersion in the polymer matrix. Two-dimensional fillers also promote the scattering of carriers, which delays the breakdown and improves the breakdown performance of composite dielectrics.

For the negative correlation between breakdown field strength and dielectric constant, many macro-regulations of polymer-based composite dielectrics are also investigated based on the development of polymer-based composite dielectric macro-control measures. Sandwich structures and composite dielectric structures with up to tens of layers are developed. The dielectric layers with different filler contents are designed to regulate the spatial distribution of the electric field, restricting the local weak electric field to a low filler content layer to inhibit the breakdown process of the dielectric. A high filler content layer enhances the dielectric constant of the composite dielectric. In addition, the use of layered films with a combination of linear and nonlinear dielectrics is expected to achieve a simultaneous increase in energy density and efficiency.

As capacitors are widely used in high-power energy storage scenarios such as aerospace and electric vehicles, higher requirements are placed on the thermal stability and dielectric properties of dielectrics at high temperatures. The high conduction loss of polymer-based dielectrics at high temperatures severely weakens their energy storage performance. A major strategy that can reduce the conductivity loss at high temperatures is to introduce wide bandgap inorganic fillers such as boron nitride nanosheets and alumina nanosheets into the polymer matrix. Another strategy is to apply wide bandgap inorganic coatings on the film surface to increase the potential barrier at the electrode-dielectric interface and hinder charge injection. An idea to enhance the high-temperature energy storage performance of composite dielectrics is the structural modification of polymer molecular chains such as grafting or cross-linking treatments, which introduces charge-trapping sites and hinders charge transport, thus suppressing the conductivity loss at high temperatures.

Summary and prospects Micro-structural and macro-structural designs both can enhance the energy density of polymer-based dielectrics. However, there are still some issues to be further addressed, namely, the interfacial interaction mechanism between filler and polymer and the breakdown mechanism of the layered structure. The carrier dissipation and heat accumulation at high temperatures are also aspects to be explored. In summary, the investigation of the interfacial bonding and breakdown mechanism of polymer-based composite dielectrics and the enhancement of the high-temperature energy storage performance of composite dielectrics will promote the dielectric capacitors to achieve broader application prospects.

Keywords structural design; interface engineering; high energy density; composite dielectrics