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熔盐体系及有关应用的新进展

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摘要: 介绍近年来熔盐体系的概况, 着重室温熔盐的发展. 熔盐在电化学制备合金和功能材料、能源、分析和分离、用作反应介质和催化剂、环境保护等方面应用前景良好.

关键词: 熔盐体系; 离子液体; 合金; 功能材料; 电池; 反应介质和催化剂; 分析和分离; 环境保护

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熔融盐是一类非水溶剂, 作为反应介质和电解介质, 用于电解冶金、表面处理、电池、能源、合成化合物材料、原子能体系等领域. 20 世纪期间, 熔盐电化学已在国民经济和科学技术中发挥了很大的作用. 本世纪, 熔盐电化学与技术必将继续蓬勃地发展^[1]. 近年来, 为了减少化学物质对环境的污染, 尽量降低挥发性有机物反应介质的消耗, 离子液体或接近常温的有机熔盐可望取代传统的有机溶剂, 用于催化合成、分离和电化学过程^[2]. 因此, 离子液体或接近常温的熔盐成为熔盐化学研究的热点之一.

1 熔盐体系

1.1 常温熔盐

广泛采用的熔盐体系大多是盐类的低共熔体. 在低限的情况下, 例如季铵盐与金属盐的混合物能形成常温熔盐, 因而这类离子液体属于深度低共熔溶剂 (Deep Eutectic Solvent, DES). 离子液体通常指室温或低温下为液体的盐, 由含氮、磷有机阳离子和大的无机阴离子组成. 常温下的离子液体又称为常温熔盐或室温熔盐 (RTMS). 形成 DES 的设想已推广到某些对水不敏感的金属氯化物, 如 $ZnCl_2$ 、 $SnCl_2$ 和 $FeCl_3$. $ZnCl_2$ 与一些取代季铵盐 (如胆碱氯化物) 的混合物能大幅度降低其凝固点, 已被大规模用作电镀锌浴和 Diels-Alder 反应的催化剂^[3].

最常用的季铵盐是烷基铵盐、烷基磷酸盐, 所含的阳离子如 N,N -二烷基咪唑阳离子 (咪唑阳离子又称咪唑鎓) 和 N -烷基吡啶阳离子 (吡啶阳离子又称吡啶鎓); 其阴离子通常是卤素离子、 ACl_4^- 以及含氟、含磷、含硫的各种离子, 如 BF_4^- 、 PF_6^- 、 $CF_3SO_3^-$ 等. 20 世纪 90 年代以前, 离子液体主要是由 ACl_3 与 1-乙基-3-甲基咪唑氯化物 (EMIC, $EtMeImCl$ 或 $emim^+Cl^-$) 或正丁基吡啶氯化物 (BPC) 组成的体系; 90 年代先后出现第一个水稳定的 $EMBE_4^+$ (1-乙基-3-甲基咪唑四氟硼酸盐)、 $EMPF_6$ 和含 $N(CF_3SO_2)_2^-$ 的咪唑类液体^[4].

21 世纪以来, 离子液体得到更迅速的发展. N,N -二乙基- N -甲基- N -(2-甲氧基乙基) 铵四氟硼酸盐 (DEMEBE₄) 比 $EMBE_4^+$ 有更宽的电位窗 (6.0 V) 和较高的离子电导率 (25 °C 时为 $4.8 \text{ mS} \cdot \text{cm}^{-1}$), 它是电化学电容器的实用离子液体^[5]. 1-乙基-3-甲基咪唑-三(三氟甲磺酰)酰亚胺锂 (EMI-LiTFSI) 熔盐在 25 °C 时的电导率为 $7 \text{ mS} \cdot \text{cm}^{-1}$, 可用作锂电池的溶剂^[6]. 1-乙基-3-甲基咪唑的氧五氟钨酸盐 ($EMWOF_5$) 在水溶液中是稳定的室温离子液体, 298 K 时它的电导率为 $3.0 \text{ mS} \cdot \text{cm}^{-1}$ ^[7]. 有配位能力的 $N(CN)_2^-$ 类离子液体具有低粘度和高电导率, 而且能溶于水. 此外, 在生物学领域以 DNA 作为阴离子的离子液体可用于研究电子信息传导^[8].

季铵盐体系的物理化学性质已有较系统的研究^[4]. 这个体系显示强过冷倾向, 例如 $\text{PMe}_3\text{H}^+\text{Cl}^-$ 的熔点为 60°C , 固化温度为 -140°C . 季铵盐体系的离子液体密度为 $1.2 \sim 1.5 \text{ g} \cdot \text{cm}^{-3}$; 粘度 $30 \sim 50 \text{ mPa} \cdot \text{s}$; 电导率 $0.1 \sim 1.4 \text{ mS} \cdot \text{cm}^{-1}$; 扩散系数 $10^{-11} \sim 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$; 稳定电化学窗口为 $2 \sim 6 \text{ V}$. 双电层电容为 $11 \sim 12 \mu\text{F} \cdot \text{cm}^{-2}$. 季铵盐离子液体的电声和电渗也有研究^[9].

季铵盐与酰胺(包括尿素)或羧酸的低共熔混合物显示不寻常的性质, 例如能明显溶解对许多“不溶的”金属氧化物, 可望应用于金属抽提^[3]. 羧酸和多种季铵盐能形成深度低共熔体, 其物理性质类似离子液体. 在这些混合物中, 电荷传递主要由离子淌度控制. 这类低共熔物容易纯化, 不与水反应, 而且多数是无毒、生物能分解的.

胆碱氯化物与尿素形成的低共熔混合物, 其凝固点为 12°C , 常温下是液体. 这种低共熔体可作为非挥发性反应介质, 例如合成新型配位聚合物 $[\text{Zn}(\text{Q}(\text{PCH}_2\text{CQ}))_2] \cdot \text{NH}_4$ 晶体^[2].

二(三氟甲磺)酰亚胺锂(LiFSI)和乙酰胺形成低共熔物(熔点为 -67°C), 其氧化和还原电位分别为 4.4 和 0.7 V (vs Li^+/Li)^[10]. LiFSI与尿素及其衍生物能形成一系列室温熔融盐, 其中 LiFSI甲基脲体系的共熔温度最低, LiFSI尿素体系的电导率最高^[11]. 二(三氟乙基磺)酰亚胺-乙酰胺体系的低共熔温度为 -57°C , 0°C 时的电导率达到 $1.27 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$, 氧化和还原电位分别为 3.8 和 0.6 V ^[12].

尿素以及许多含氢键化合物, 如酸、胺和醇与某些碱金属卤化物形成熔点在 $30 \sim 140^\circ\text{C}$ 之间的低共熔物^[13], 如尿素- $\text{NaBr} \cdot \text{KB}$ 低共熔体的熔点为 51°C , 乙酰胺-尿素低共熔体的熔点为 56°C ^[14], 两者形成的乙酰胺-尿素- $\text{NaBr} \cdot \text{KB}$ 的熔体可在接近常温下使用.

1.2 低温熔盐和高温熔盐

室温熔盐、低温熔盐、高温熔盐之间并无明显的界限, 本文所指的低温熔盐是使用温度范围约在 $100 \sim 250^\circ\text{C}$ 内的熔盐.

尿素- NaCl 及尿素- $\text{NaBr} \cdot \text{KB}$ 低共熔体已分别用于电沉积锌合金、钛合金、稀土合金^[15], 使用温度 125°C 、 100°C .

AlCl_3 - NaCl 和 AlCl_3 - $\text{NaCl} \cdot \text{KCl}$ 熔融盐体系是近年来研究较多的无机熔融盐体系, 前者的使用温

度为 $180 \sim 250^\circ\text{C}$, 后者可在较低温度下使用. 此外, 还有 ZnCl_2 - $\text{NaCl} \cdot \text{KCl}$ 低共熔体. 这类低温熔盐主要用于电沉积活泼金属及其合金, 如铝、钨、铝、铝合金等.

常用的高温熔盐体系为 $\text{LiCl} \cdot \text{KCl}$ (使用温度: $400 \sim 450^\circ\text{C}$)、 $\text{NaCl} \cdot \text{KCl}$ ($700 \sim 750^\circ\text{C}$) 和 $\text{LiF} \cdot \text{KF}$ ($670 \sim 750^\circ\text{C}$), 此外还有 CaCl_2 - NaCl ($550 \sim 650^\circ\text{C}$)、 $\text{KCl} \cdot \text{NaCl} \cdot \text{MgCl}_2$ ($600 \sim 650^\circ\text{C}$)、 $\text{NaCl} \cdot \text{KCl} \cdot \text{NaF}$ ($700 \sim 750^\circ\text{C}$). 这些体系主要用于电沉积难熔金属、稀土金属及其合金, 电解制取超导体膜、半导体膜, 以及分离放射性金属等. 此外, 还有用于燃料电池的熔融碳酸盐.

2 熔盐在电化学及有关领域中的应用

2.1 电化学制备金属和合金、表面功能膜

应用季铵盐-金属盐体系电沉积金属和合金已有许多研究, 例如: 在碱性 1-乙基-3-甲基咪唑氯化物-四氟硼酸盐离子液体中电沉积 Pd-In-Pd-Ag 合金^[16]; 在 AlCl_3 -1-丁基-3-甲基咪唑氯化物和 1-丁基-3-甲基咪唑六氟磷酸盐熔盐中电结晶 Ni-Co 沉积物的大小在纳米尺度范围内^[17]; 用脉冲电镀法在 AlCl_3 -BPC-NiCl₂ 熔盐中, 于铂和软钢电极上沉积光亮的 Ni-Al^[18]; 在 1-甲基-3-丁基咪唑鎓的二(三氟甲磺)盐- TiCl_4 中电沉积钛, 循环伏安法、计时安培法和扫描隧道显微镜研究表明, 金基底首先与钛合金化^[19].

作者于近年研究了在接近常温的乙酰胺-尿素- $\text{NaBr} \cdot \text{KB}$ 熔盐中, 电沉积纳米结构 Nd-Co-Nd-Fe^[20]、Sn-Co^[21]、Nd-Co-Fe-Tb-Dy-F 等稀土-铁族 (RE-Fe) 合金膜, 测定它们的矫顽磁力、剩余磁感应强度和饱和磁感应强度. 在尿素低温熔体中容易得到纯的 RE-Fe 所得 Sn-Co 膜不含氧; 而水溶液沉积的 Sn-Co 最大含氧量却达到 50% (by at cm)^[22].

使用在 100°C 的尿素- $\text{NaBr} \cdot \text{KB}$ 或尿素- NaBr 熔盐能够电沉积出稀土含量相当高的稀土-铁族合金膜, 例如 Tm-Co^[23]、La-Ni^[24]、Gd-Ni^[25]、Sm-Fe^[26]. 而在尿素- $\text{NaBr} \cdot \text{KB}$ 或 125°C 的尿素- NaCl 熔盐中又已电沉积了钛合金膜, 例如 Ti-Zr-Ti-Ni^[27]. 在 250°C 的 ZnCl_2 - $\text{NaCl} \cdot \text{KCl} \cdot \text{KF}$ 中, 电沉积出金属钨膜、钼膜^[28], 在 AlCl_3 - NaCl 熔盐中电沉积得到耐蚀的纳米 AlMn 合金镀层^[29].

电沉积使用高温熔盐体系比较多. 已有的研究包括: DyCl_3 在 LiCl-KCl 熔体中的电极反应及 Dy 的电结晶^[30]; 测定了 Pr(III) 在 LiCl-KCl 低共熔体和 $\text{CaCl}_2\text{-NaCl}$ 熔体中的 D° 、 β 和 α ^[31]; 计算 ErAl_3 的标准生成自由能^[32]; 用 Fe-Cr-N 电极, 在 LiCl-KCl 熔体中电化学制取了 Sm-Ni 、 Yb-Ni 、 Dy-Fe 、 Gd-Co ^[33] 等合金膜. 20 世纪 80~90 年代, 国内已在 NaCl-KCl 氯化物熔体中电解制取了许多稀土合金及表面合金膜, 例如 Nd-Fe 、 Gd-Cr 、 Dy-Ni 、 Y-Ba-Cu ^[34-37], 并研究了电极过程及形成合金的机理、测定稀土原子在其合金相中的扩散系数和金属间化合物的生成自由能^[38].

难熔金属的电解制备研究也占有重要的地位, 例如在熔盐中直接电解还原固态金属氧化物提炼金属、制取合金. 现已成功地制备了钛及钛合金、硅及硅合金^[39]. 又如在 LiCl_2O 中电解还原 Nb_2O_5 制取了金属铌粉; 在 $\text{LiCl}_3\%$ (by mass) Li_2O 熔体中电化学还原 U_3O_8 粉制取铀; 在 1123 K 的 CaCl_2 中直接电解还原固体 SiO_2 制备太阳能级硅; 研究钽在熔融碱性氟化物中的电化学成核, 以优化制取钽覆盖层的操作条件^[40].

此外, 还应用电化学方法制备其它功能性薄膜. 例如: 在饱和了 SCl_4 的 1-丁基-1-甲基吡咯的二(三氟甲基磺酰)酰亚胺盐的室温熔盐中, 电沉积的纳米硅层^[41]; 在接近常温的尿素熔盐体系中电沉积纳米 Zn-Sb_3 半导体^[42]; 在熔融 $\text{LiCl-KCl-Li}_3\text{N}$ 中电合成制取氮化物催化剂的 Mg_3N_2 膜^[43]; 在 MgB_2O_4 、 KCl-NaCl 和 MgCl_2 熔融混合物中电镀 MgB_2 超导体膜^[44]; 在的 $\text{KBF}_4\text{-KF}$ 熔体中镍板上电沉积得到非晶 P 型硼晶片^[45]; 在 $\text{NaCl-KCl-NaF-K}_2\text{TiF}_6\text{-K}_2\text{SiF}_6\text{-KBF}_4$ 熔盐中电化学合成了 $\text{Ti}_3\text{Si}_3\text{B}$ 化合物^[46]; 在含有 TeCl_4 的 LiCl-KCl 中, 在 Zn 基底上进行电化学离子交换反应得到 ZnTe 半导体膜^[47]. 研究氮化物在 $\text{LiCl-KCl-Li}_3\text{N}$ 熔盐中的电化学, 提供再生氮化物燃料的电化学数据和电化学形成功能氮化物膜的新工艺^[48].

2.2 熔盐在能源、防腐、分析测试等方面的应用

室温熔盐应用于电池的实例: 用 LiFSO_3 或季铵盐基的离子液体作电解质组成的锂离子电池^[49-51]; 用 BMI-PE_6^- 和 $\text{BMI}(\text{CF}_3\text{SO}_2)_2\text{N}^-$ 两种憎水的离子液体提高锂-海水电池的效率^[52]; 由离子

液体和胶凝体组成的电解质改善染料敏感太阳能电池的耐用性能^[53]; 用对称四烷基磷碘化物熔体作为染料敏感纳米晶太阳能电池的电解质^[54]; 热电池通常采用碱金属卤化物低共熔物作为熔融电解质, 其它如硝酸盐、醋酸盐、乙酰胺、尿素、四烷基铵盐等等^[55]. 高温熔盐可用来制备电极材料或作电解质, 例如: 在 LiCl 或 LiNO_3 的熔盐流体中制备用作锂电池的阴极材料的尖晶石型锰酸锂晶体^[56]; MgCl_2 熔盐处理 LiCO_2 表面, 改善锂离子电池阴极的性能^[57]; Adams 热体系采用熔融碳酸盐作为电解质组装千瓦级燃料电池^[58]. 用高比表面积和离子液体组装双电层电容器, 电容高达 $180 \mu\text{F/g}$; 以含 BF_4^- 阴离子的离子液体作电容器电解质, 性能也很好^[59]. 用铁阳极在 NaOH-KOH 熔体中制备了高铁酸盐 (FeO_4^{2-}), 可望用于高能密度可再充电池、绿色合成化学以及处理污染物和毒物^[60].

在熔盐体系中制备出多种耐蚀、耐磨和抗氧化材料. 例如: 在 $\text{LiCl-KCl-Li}_3\text{N}$ 熔盐中 Al 阳极极化, 形成具有优越耐磨性和耐腐蚀性的 AlN 膜^[61]; 在高温熔盐中于 Nb-S 基底上沉积 C 修饰的硅化物能改善抗氧化性能^[62]; 在熔融 $\text{AlCl}_3\text{-NaCl-KCl}$ 体系中电沉积 Al-C 或 Al-N 合金, 改善 TiAl 金属间化合物的抗氧化性能^[63]; 在熔融 NaCl-TiCl_4 中, 接触沉积耐腐蚀性优于不锈钢的富钛合金层^[64]; 在 LiF-NaF-KF 熔盐中钼基底上电沉积 TiB_2 保护层^[65].

在熔盐介质中制备其它功能材料, 诸如: 在 $\text{NaCl-NaF-Na}_3\text{SiF}_6$ 熔体中多晶基底上生长用作光电材料的 $\beta\text{-FeSi}_3$; 用 $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4$ 混合物熔盐流合成 $\text{LaB}_6/\text{Ti}_3\text{FeC}_5$ 高纯铁电层^[66-67]; 在 NaCl-KCl 中制备 ZnNb_2O_7 微波电介质材料、合成镧掺杂钛酸盐陶瓷^[68]; 熔融 K_2CO_3 、 LiOH 、 NaOH 分别与金属 N 形成各种复合蓄热材料^[69]; 用离子液体制作 Li^+ 离子导电的电着色器件^[70]; 在高温氯化物熔盐中制取电催化的 NO 纳米粒子、磁性纳米 Co_3O_4 棒^[71-72].

高温核反应器的熔盐反应器可用于发电和供制氢所需的热, 并可用来处理熔融氟化物中的铀或其它超铀元素^[73]. 测定锕系离子和镧系离子的活度系数和扩散系数, 以便分离氯化物、氟化物熔体中的锕系和镧系元素^[74-76].

离子液体可用于制作电化学传感器,例如多孔聚乙烯膜(渗入 $[C_2MM][BF_4]$)覆盖的电极组成安培传感器检测 O_2 。用离子液体作敏感材料制造石英结晶微天平传感器,检测甲苯、甲醇、乙醇、2-丙醇、1-丁醇、丙酮、乙腈、氯仿、四氢呋喃和乙酸乙酯等多种有机蒸气^[77]。室温离子液体也用于制作光学传感器,检测气态和溶解的 CO_2 ^[78]。在亲水的 $[bmim][BF_4]$ 中得到活性好的山葵过氧化酶,适用于在非水溶液生物催化和生物传感器^[79]。

此外,离子液体型碳糊电极在物理化学和电分析化学领域有良好的应用前景;由离子液体膜修饰的碳微电极可用于测定离子液体中 $Fe(CN)_6^{3-}$ 的浓度^[80-81]。

2 3 离子液体的应用

离子液体在化学领域中的应用大致包括:(1)作为化学惰性物质,即用作电解质、萃取剂、表面活性剂、手性介质;(2)催化剂;(3)溶剂介质,包括化学分离、有机合成反应。近年来,国内外对离子液体的反应及其催化作用的研究相当活跃^[82-83]。

在加成、氧化、还原、氯化、烷基化、氨化、重排、缩合、偶联、环氧化、卤化、重氮化等反应中,离子液体作为介质或催化剂显示出其优势^[83-88]。用离子液体作溶剂时,反应速率、选择性和产率都优于传统的溶剂,而且产品易分离,溶剂可回收再用。离子液体用作催化剂时,催化活性有明显提高,催化剂容易循环使用。

离子液体的蒸气压很小可忽略、热稳定性好、能溶解许多有机化合物和无机化合物,可以抽提许多有机化合物和金属离子。例如:从水中萃取甲苯、苯胺、苯甲酸、氯苯、 Cd^{2+} 、 Hg^{2+} ;在 $[bmim]B$ 溶液中微波辅助萃取虎杖根茎的白藜芦醇;用1-甲基-3-辛基咪唑鎓氯化物膜从 n -庚烷分离甲苯;用咪唑鎓基离子液体从缓冲水溶液抽提青霉素 G 。离子液体还被应用于毛细管电泳、气相色谱、液相色谱^[89-92]。

为了减少温室效应和利用 CO_2 作为 C 化学的原料,必须研究吸收和转化 CO_2 的有效方法。用离子液体固定和转化 CO_2 更环保和更简单,而且 CO_2 溶解度明显比普通有机溶剂高^[93]。采用离子液体电化学合成环酯开辟了有机合成的新途径^[94]。

此外,室温熔盐也应用到生物方面,例如:在离子液体中的生物催化,开发非水酵素化学的新领

域^[95];以离子液体作为介质,电催化制备类磺酮苷的亲脂衍生物^[96]。

3 结 语

进入21世纪以来,熔盐(尤其是室温熔盐)发展很快,而且应用范围日益宽广,涉及国民经济、国防科技、环境保护等领域。为了继续发展熔盐体系,迫切需要深入了解熔盐的性质及有关理论基础,开拓合成熔盐的新方法和新体系。最近已有文献报道包括了含氟阴离子的烷基咪唑鎓基离子液体结晶结构、光谱和衍射研究;用力场完成一系列室温离子液体的分子动力学模拟;基于动力学参数设计绝热循环反应器连续制备离子液体;制取对磁场有强烈的响应、具有高电导率和催化性能磁性离子液体;合成一类很有前途的含有脂肪族四烷基铵二阳离子和TFS阴离子的电解质等实例^[97-101]。

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Molten Salt Systems and the New Developments for the Application of Molten Salts

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Abstract: The general situation of molten salt systems since 21 century are presented. The development of room temperature molten salts are emphasized. Applications of molten salts to the areas of preparing alloys and functional materials, batteries and capacitors, analysis and separation, use as reaction media and catalyzers, environmental protection have good prospect. In order to continually develop the molten salt system, it is necessary further to know the properties of molten salts and relevant theories, as well as exploiting the new methods and novel systems of synthesizing molten salts.

Key words: molten salt systems, ionic liquids, alloys, functional materials, batteries, reaction media and catalyzers, analysis and separation, environmental protection