季铵化杂萘联苯聚芳醚酮酮离子交换膜制备与性能

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摘要 离子交换膜是全钒氧化还原液流电池的主要部件之一, 其选择性和稳定性在一定程度上决定了电池的寿命, 而目前大多数离子交换膜存在选择性或稳定性欠佳的情况. 为了制备全钒氧化还原液流电池用高选择性离子交换膜, 本文将不同溴甲基含量(0.75~0.99, 平均每摩尔重复结构单元含有溴甲基的摩尔数)的含溴甲基杂萘联苯聚醚酮酮(BPPEKK)通过溶液浇铸法制备基膜, 之后在三甲胺水溶液中进行胺化得到季铵化杂萘联苯聚醚酮酮阴离子交换膜(QBPPEKK). 测试了QBPPEKK的离子交换容量、吸水率、溶胀率、钒渗透系数和面电阻. 随着BPPEKK溴甲基含量的增加, 所得QBPPEKK膜的离子交换容量和含水率增加, 而其面电阻和钒离子质量传递系数降低. 将QBPPEKK膜组装于全钒氧化还原液流电池中, 电池的电压效率(VE)和能量效率(EE)随着QBPPEKK膜离子交换容量的增加而上升; 当BPPEKK的取代度为0.99时, 所制得的阴离子交换膜为QBPPEKK90膜, 由其组装成电池的EE为87.7%(电流密度为40 mA/cm²), 大于同条件下Nafion117的数值(86.0%). 在1.5 mol/L的VO₂⁺溶液中浸泡60 d后, QBPPEKK膜的拉伸强度高于36 MPa、膜表面形貌没有明显变化、组装电池性能变化不大, 结果表明QBPPEKK膜在VO₂⁺溶液中表现出良好的稳定性.

关键词 杂萘联苯聚芳醚酮酮, 溴甲基, 季铵化, 离子交换膜, 钒电池

作为一种大型储能装置, 全钒氧化还原液流电池(VRB, 简称钒电池)可用于解决能源产生端和使用端之间不匹配的问题以及不连续可再生能源的储存^[1~7]. 钒电池具有设计灵活、可以深度充放电、电池效率高等优点^[1,2,5~7]. 作为组成部分之一的隔膜在VRB中起着分隔正、负极电解液, 防止电解液交叉渗透, 传导特定离子构成电流回路的作用^[6,8~11]. 杜邦公司的Nafion系列膜因具有良好的导电性和化学稳定性被广泛地应用于钒电池中, 但其阻钒性能较差, 容易造成电池容量的损失; 而且Nafion系列膜高昂的价格也成为其商业化应用的阻碍^[12~15]. 一些研究者基于Nafion膜做了一定的修饰, 一定程度地提高了Nafion膜的阻钒性能, 但是改性之后的膜仍然无法摆

脱成本高的问题. 一些研究者基于不含氟聚合物制备了阳离子交换膜^[16~18], 与Nafion系列相比, 这些阳离子交换膜的成本和钒渗透系数有所下降, 但是阳离子交换基团的存在限制了其阻钒性能进一步提升. 而阴离子交换膜应用于钒电池中, 道南效应能阻止钒离子交叉渗透, 降低电池的容量损失, 提高钒电池的综合性能^[19,20]. 因此, 开发新型钒电池用阴离子交换膜具有重要的研究和实用价值.

由本课题组研发的二氮杂萘酮含有非共平面扭曲结构, 其具有良好的机械和化学稳定性, 且在常用的制膜溶剂中可溶解, 是一种具有广泛应用前景的高性能膜材料. 基于这一结构制备了一系列离子交换膜, 其在钒电池中表现出较好的性能^[20~25]. 本文

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主要制备了季铵化杂萘联苯聚醚酮酮(QBPPEKK)阴离子交换膜,考察其基本性能及其在全钒液流电池中的电池效率和稳定性.

1 实验

(i) 试剂与仪器. 含溴甲基杂萘联苯聚醚酮酮(BPPEKK, 根据文献[23]制备), 溴甲基含量为0.75, 0.85和0.99(平均每摩尔重复结构单元含有溴甲基的摩尔数), 分别标记为BPPEKK70, BPPEKK80和BPPEKK90; *N*-甲基吡咯烷酮(NMP)、33%三甲胺水溶液、硫酸氧钒(VOSO_4)等均为市售分析纯; BTS系列5V/3A电池检测系统(深圳市新威尔电子有限公司); CHI604D电化学工作站(上海辰华仪器有限公司).

(ii) 季铵化杂萘联苯聚醚酮酮离子交换膜的制备. 将干燥的含溴甲基杂萘联苯聚醚酮酮BPPEKK溶解于NMP中形成10 wt%(质量百分比)的铸膜液, 60℃下在玻璃板上刮制成膜. 将基膜放入三甲胺水溶液中, 40℃浸泡反应48 h, 取出用稀盐酸(5 wt%)处理即得到季铵化杂萘联苯聚醚酮酮离子交换膜(QBPPEKK), 反应简式如图1所示.

(iii) 测试. 文献[23]所提方法测定QBPPEKK膜的离子交换容量(IEC). QBPPEKK膜(质量为 m)浸泡在 NaNO_3 溶液(0.1 mol/L)中2 d后, 以铬酸钾溶液(10 wt%)为指示剂, 用 AgNO_3 溶液(浓度为 C_{AgNO_3} , 体积为 V_{AgNO_3})滴定, 通过下式即可计算IEC:

$$\text{IEC} = \frac{V_{\text{AgNO}_3} \times C_{\text{AgNO}_3}}{m}. \quad (1)$$

测量在去离子水中平衡48 h过程中QBPPEKK膜的质量及尺寸变化^[23], 根据公式(2)和(3)计算其吸水率(W_c)和溶胀率(swelling ratio):

$$W_c = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%, \quad (2)$$

$$\text{溶胀率} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\%, \quad (3)$$

其中, W_{wet} 和 L_{wet} 是湿膜重量和尺寸, W_{dry} 和 L_{dry} 是干膜重量和尺寸.

采用交流阻抗法对QBPPEKK膜的面电阻进行测试^[23], 测试所用的溶液是2.0 mol/L VOSO_4 +3.0 mol/L H_2SO_4 . 分别测试电池在有膜时的总电阻 R_1 和无膜时溶液的电阻 R_2 , 通过下式即可得到膜的面电阻:

$$R = (R_1 - R_2) \times S, \quad (4)$$

其中, S 为QBPPEKK膜的有效面积.

采用自制渗透池测试QBPPEKK膜的钒离子质量传递渗透系数, 测试方法如文献[23]所述, 用膜样品(有效面积: 1.78 cm²)将左右半池分开, 其中分别装30 mL的1.0 mol/L VOSO_4 +2.5 mol/L H_2SO_4 溶液和1.0 mol/L MgSO_4 +2.5 mol/L H_2SO_4 溶液. 周期性地测试 MgSO_4 端溶液吸光度. 根据公式(5)计算钒离子质量传递系数(K_s):

$$\ln[B-2A] = \ln[absB] - 2K_s St/V, \quad (5)$$

图1 QBPPEKK的制备反应式

Figure 1 Synthesis of QBPPEKK

式中, A 是 MgSO_4 端溶液吸光度, B 是 VO_2SO_4 端溶液吸光度, S 是膜有效面积, V 是所用溶液体积。

参照文献[23]对QBPPEKK膜在钒电池中的效率进行测试。两极电解液分别是1.5 mol/L $\text{VO}_2^{2+}/\text{VO}_2^{3+}$ +3.0 mol/L H_2SO_4 溶液和1.5 mol/L $\text{V}^{2+}/\text{V}^{3+}$ +3.0 mol/L H_2SO_4 溶液。膜样品的有效面积为5 cm²。

2 结果与讨论

2.1 QBPPEKK阴离子交换膜基本性能

如表1所示, BPPEKK的溴甲基含量从0.75增加到0.99, 溴甲基完全反应转化为季铵基后, 所得QBPPEKK膜的理论离子交换容量 IEC_T 应从1.26增至1.6 mmol/g, 而实际测得QBPPEKK膜的IEC从1.15 mmol/g增至1.51 mmol/g, 说明溴甲基的胺化反应虽然不完全, 但溴甲基胺化反应转化率高于91%。这是因为胺化反应发生在三甲胺溶液与BPPEKK基膜的溴甲基之间, 固相中的溴甲基基团活动受到限制, 导致胺化反应很难完全进行。

表2列出了QBPPEKK膜的基本性能, 从表中可以看出, 当QBPPEKK膜的IEC从1.15 mmol/g增加到1.51 mmol/g时, 含水率从15.7%增加到20.1%, 溶胀率从8.2%增大到11.5%。这是因为IEC增加, QBPPEKK膜的亲水性增强, 吸水率和溶胀率相应增大, 相对较小的溶胀率表明其具有较好的尺寸稳定性; 随着IEC的增加, QBPPEKK膜面电阻从1.10 $\Omega \text{ cm}^2$ 下降至0.63 $\Omega \text{ cm}^2$, 因为随着膜的IEC增加, 膜的离子传导能力增强, 面电阻降低。QBPPEKK膜中的季铵基与溶液

中钒离子之间存在道南排斥作用, 使得其钒离子质量传递系数(K_s)低于Nafion117膜的1/2, 表现出良好的阻钒性能。

2.2 QBPPEKK膜的电池性能

从表3中可知, QBPPEKK膜组装钒电池的库伦效率在98%以上, 高于Nafion117膜(95.9%), 这主要是因为QBPPEKK膜的钒离子渗透性低于Nafion117膜, 表现出较好的阻钒性能, 使其组装的电池具有较高的库伦效率。当IEC从1.15 mmol/g增加到1.51 mmol/g时, QBPPEKK膜组装钒电池的电压效率从86.6%升高到89.3%, 接近Nafion117的电压效率(89.7%), 这是由于IEC增加膜的离子传导性随之增加而面电阻降低, 使得其电池的电压效率提高。由QBPPEKK90膜组装钒电池的能量效率可达87.7%, 与IEC相近的QBPPEKK80膜组装钒电池的能量效率(88.0%)^[23]相当, 高于Nafion117膜的值(86.0%)。

考察了QBPPEKK90和Nafion117膜在不同电流密度(20~80 mA/cm²)下的电池效率。从图2可知, 随着电流密度的增大, QBPPEKK和Nafion117组装电池的库伦效率均增加。因为, 在高电流密度下, 较短的循环时间有效地减少了钒离子的渗透, 提高了库伦效率。当电流密度从20 mA/cm²增加至80 mA/cm²时, QBPPEKK膜的库伦效率从97.1%增加至99%, 均高于相同测试条件下Nafion117膜的库伦效率。QBPPEKK和Nafion117膜的电压效率均随着电流密度增加而降低, 高电流密度下严重的极化现象导致了电压效率降低。在相同电流密度下(20~80 mA/cm²), QBPPEKK90

表1 QBPPEKK膜的IEC

Table 1 IEC of QBPPEKK membranes

聚合物	溴甲基含量	阴离子交换膜	$\text{IEC}_T(\text{mmol/g})$	IEC(mmol/g)
BPPEKK70	0.75	QBPPEKK70	1.26	1.15±0.05
BPPEKK80	0.85	QBPPEKK80	1.41	1.30±0.04
BPPEKK90	0.99	QBPPEKK90	1.60	1.51±0.04

表2 QBPPEKK膜的基本性能

Table 2 Properties of QBPPEKK membranes

膜	吸水率(%)	溶胀率(%)	面电阻($\Omega \text{ cm}^2$)	$K_s \times 10^5(\text{cm/min})$	厚度(μm)
QBPPEKK70	15.7	8.2	1.10±0.12	5.0	46
QBPPEKK80	18.6	8.9	0.79±0.10	3.1	45
QBPPEKK90	20.1	11.5	0.63±0.11	2.3	44
Nafion 117	19.6	15.0	0.54±0.08	11.9	190

表3 QBPPEKK膜的钒电池效率^{a)}

Table 3 Efficiencies of VRB with QBPPEKK membranes

膜	库伦效率(%)	电压效率(%)	能量效率(%)
QBPPEKK70	98.6	86.6	85.3
QBPPEKK80	98.4	88.0	86.5
QBPPEKK90	98.2	89.3	87.7
QBPPEKK80 ^[23]	98.6	89.2	88.0
Nafion117	95.9	89.7	86.0

a) 电流密度40 mA/cm²

膜组装电池表现出了与Nafion117相当的能量效率。

2.3 QBPPEKK膜在钒电池中的稳定性

如表4所示,在1.5 mol/L VO₂⁺+3.0 mol/L H₂SO₄溶液中浸泡60 d后, QBPPEKK膜拉伸强度略有降低,拉伸强度高于36 MPa, 仍然保持较好的机械性能,表明QBPPEKK膜在五价钒溶液中具有较好的稳定性。图3为浸泡前后QBPPEKK90膜表面形貌的扫描电子显微镜(SEM)照片,由图可知,浸泡60 d后的QBPPEKK膜表面形貌(图3(b))没有明显变化,依然光滑平整,表明QBPPEKK膜没有发生明显腐蚀。

表4 QBPPEKK膜的机械性能

Table 4 The mechanical properties of QBPPEKK membranes

膜	浸泡前		浸泡60 d	
	拉伸强度(MPa)	断裂伸长率(%)	拉伸强度(MPa)	断裂伸长率(%)
QBPPEKK70	48	34	42	25
QBPPEKK80	52	39	41	30
QBPPEKK90	45	22	36	34

图3 在VO₂⁺溶液中浸泡60 d前后QBPPEKK90膜的表面微观结构。(a) QBPPEKK90; (b) 浸泡后QBPPEKK90

Figure 3 SEM images of QBPPEKK90 membrane before and after immersed in VO₂⁺ solution for 60 d. (a) QBPPEKK90; (b) QBPPEKK90 after immersed for 60 d

图2 (网络版彩色)QBPPEKK90和Nafion117膜的单电池性能(20~80 mA/cm²)

Figure 2 (Color online) Cell efficiencies of QBPPEKK90 and Nafion117 (20~80 mA/cm²)

图4为VO₂⁺溶液中浸泡60 d前后QBPPEKK90膜的单电池性能,由图可看出在20~60 mA/cm²电流密度下, QBPPEKK90膜在钒溶液浸泡前后的库伦效率基本没有变化,而能量效率变化差值均在1.4%以内,进一步说明QBPPEKK膜在五价钒电解质溶液中具有

图4 (网络版彩色)在VO₂⁺溶液中浸泡60 d前后QBPPEKK90膜的单电池性能

Figure 4 (Color online) Cell efficiencies of VRB with QBPPEKK90 membrane in original state and after immersed in VO₂⁺ for 60 d

较好稳定性.

3 结论

制备了含溴甲基杂萘联苯聚醚酮酮(BPPEKK)基膜, 经与三甲胺季铵化后, 得到季铵化杂萘联苯聚醚酮酮阴离子交换膜(QBPPEKK). 随着BPPEKK的溴甲基含量增大, QBPPEKK膜的离子交换容量和含水率升高, 而面电阻和钒离子质量传递系数降低,

QBPPEKK膜的钒离子质量传递系数均低于Nafion117膜. QBPPEKK膜组装钒电池的库伦效率均高于Nafion117膜, 表现出良好的阻钒性能; QBPPEKK90膜组装钒电池的能量效率为87.7%, 高于Nafion117的数值(86.0%), 表现出良好的电池性能. 通过对比在1.5 mol/L VO_2^+ 溶液中浸泡60 d前后QBPPEKK膜的机械性能、微观结构和单电池性能, 表明QBPPEKK膜在 VO_2^+ 溶液中具有良好的稳定性.

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Summary for “季铵化杂萘联苯聚芳醚酮酮离子交换膜制备与性能”

Preparation and properties of quaternized poly (phthalazinone ether ketone ketone) anion-exchange membrane for all-vanadium redox flow battery

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As one of stationary energy storage device, all-vanadium redox flow battery (VRB) could effectively balance the relationship of electricity generation and demand side, in which interests are based on having features of high efficiency, flexible design, low cost and so on. Ion exchange membrane is one of the key components of VRB, separating redox-active ions and allowing the transfer of non-reaction species. Nafion series from Dupont company could ideally satisfy the requirements of high conductivity and good stability but facing the disadvantages of poor vanadium blocking ability in VRB. Modified Nafion membranes partially conquered the problem of poor ion selectivity but still suffering from high cost. Cationic exchange membranes prepared from non-fluorinated polymers have lower vanadium ion permeability and cost while cationic exchange groups hinder the further improvement of vanadium ion blocking. On the contrary, anionic exchange membranes (AEMs) exhibit low vanadium ion diffusion coefficient because of Donnan exclusive effect. It is much of importance to explore new AEMs. And the lifetime of the VRB cell depends on the selectivity and stability of the membranes to some degree. However, most of ion exchange membranes for VRB application showed low selectivity or stability. In order to improve the selectivity of ion exchange membranes, poly(phthalazinone ether ketone ketone) containing bromomethyl moieties (BPPEKK) with varied content of bromomethyl were dissolved to prepare BPPEKK base membranes using solution casting method. Quaternized poly(phthalazinone ether ketone ketone) (QBPPEKK) anion-exchange membranes were prepared from the amination of BPPEKK membranes in trimethylamine aqueous solutions. The measured ion exchange capacity (IEC) values of QBPPEKK membranes were in the range of 1.15–1.51 mmol/g, which were lower than the theoretical IEC (IEC_T) values. The result indicated the incomplete amination reaction of bromomethyl groups with trimethylamine. Properties of QBPPEKK membranes including water uptake, swelling ratio, area resistance and vanadium ion permeability were investigated. Water uptake and swelling ratio of QBPPEKK membranes increased with the increase in content of bromomethyl in BPPEKK, while area resistance and vanadium ion permeability decreased. The vanadium ion mass transfer coefficient of QBPPEKK membranes was in the range of 2.3×10^{-5} – 5.0×10^{-5} cm/min, less than that of Nafion 117 membrane (11.9×10^{-5} cm/min). QBPPEKK membranes showed much lower vanadium ion permeability than Nafion 117. VRB with each QBPPEKK membrane showed higher columbic efficiency (CE) than the battery with Nafion117 membrane. QBPPEKK membrane with higher IEC exhibited higher voltage efficiency and energy efficiency (EE). When the content of bromomethyl reached 0.99, the VRB with QBPPEKK90 membrane had EE of 87.7% (current density: 40 mA/cm²), higher than that of Nafion117 membrane (86.0%). When the charge-discharge current density increased from 20 to 80 mA/cm², the CE of VRB with QBPPEKK90 membrane increased from 97.1% to 99.0%, and EE of VRB cell with QBPPEKK90 decreased from 91.1% to 80.2%. After QBPPEKK membranes were immersed in VO₂⁺ solution for 60 d, the tensile strength of the membranes was more than 36 MPa, which was lower than that of the original QBPPEKK90 membrane. There were no significant changes on microstructure of QBPPEKK membrane after the membrane had been immersed into 1.5 mol/L VO₂⁺ solutions for 60 d. Compared with the original QBPPEKK90 membrane, CE changed slightly and EE decreased 1.4% at the charge-discharge current density ranging from 20 to 60 mA/cm² after the membrane was immersed in VO₂⁺ solution for 60 d. The results suggested that QBPPEKK membranes showed good chemical stability.

poly(phthalazinone ether ketone ketone), bromomethyl, quaternization, ion exchange membrane, vanadium redox flow battery

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