

(19)
(12)

(KR)
(A)

(51) 。 Int. Cl. ⁷
C08G 75/00

$$\begin{pmatrix} 11 \\ 43 \end{pmatrix}$$

2003 - 0007583
2003 01 23

| | |
|------|---------------------|
| (21) | 10 - 2002 - 7014862 |
| (22) | 2002 11 06 |
| | 2002 11 06 |
| (86) | PCT/EP2001/05644 |
| (86) | 2001 05 17 |

(87) WO 2001/87992
(87) 2001 11 22

(81)

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가

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가

AP ARIPO : 가

EA :

EP :

OA OAPI : 가

(30) 10024576.5 2000 05 19 (DE)

(71) 가
가 70199, 72.

| | | | |
|------|---|----------|----|
| (72) | , | | |
| | , | 73760, | 11 |
| | , | | |
| | , | 가 70569, | 54 |
| | , | | |
| | , | 69469, | 11 |

(74)



:

(54)

, (1), Q
 , (2) (3), R 2가, a) R
 (4A), (4B), (4C), (4D), (4E), (4F), (4G) / (4H), b)
 R (5A) / (5B) 가 /가 R
 (5C) / (5D), c) R (6) (bridge),
 R, R₁, R₂, R₃, R₄, R₅, M, X, Y, Z m.

- Q - R (1)

Q, , ,

 (2)  (3),

R 2가 .
 , 가 .

(1) (polyarylene), (polystyrene), (polyvinylpyridine), (poly
 pyrene) (polyphenylenevinylene),
 , Radel() R (polysulfone), PEK
 (polybenzimidazole), (polyindophenine), (polypyrrole),
 polyazulene), (polycarbazole), (polyazole)

(polyelectrolyte membrane fuel cell) (PEM)

(proton conductor) . (membrane electrode assembly) (MEA)가 , (tolerance) 가 , (lower upper flow limit), , .

DE 196 22 337 (sulfinate) DE 196 22 337, WO 99/02755, WO 99/02756 (ionomer) () (network) 가 , , , , , .

WO 99/02756 WO 99/02755 () 가 , / () 60 90 / , 80 .

25 100 cm , , , . ing property) , 가 90 100% (swell .

가 80 , 100 .

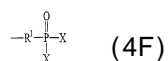
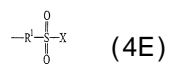
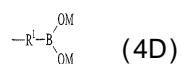
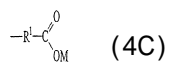
가 .

가

1

1 .

a) R (4A), (4B), (4C), (4D), (4E), (4F), (4G) / (4H)



,

R¹

1 40

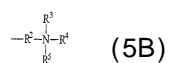
,

,

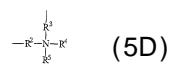
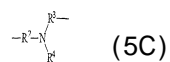
M , , Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, ,

X ,

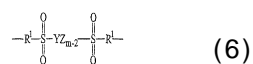
b) R (5A) / (5B) ,



R^2, R^3, R^4 R^5 1 40
 R^2, R^3, R^4
 / R (5C) / (5D) ,



c) R (6) (bridge) ,



R ,

Y 1 40 , ,

Z , ,



, H, C, O, N, S, P, , 20 g/ ,

m 2 ,

(1) ,

, 가 ,
 가 가 .

, 가 . 가 ,

(doped polymer membrane) , 25 100 cm

,

, 가 ,

가 10 $100\mu\text{m}$, 80 ,

,

,

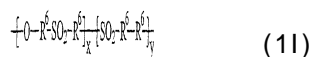
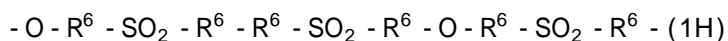
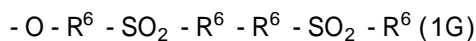
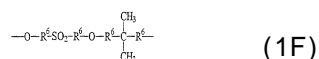
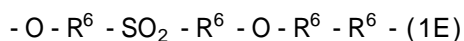
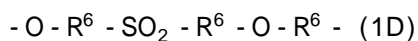
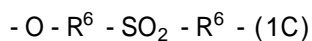
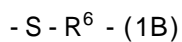
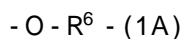
80 ,

,

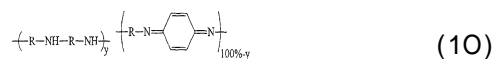
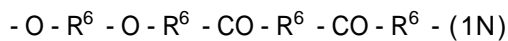
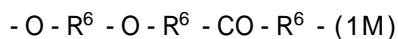
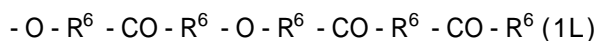
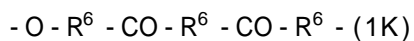
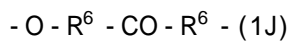
.

가
가 " " 1.0 CD Rompp Chemie Lexikon(Stuttgart/New York: Georg Thieme Verlag, 1995) ,

(1), (1A), (1B), (1C), (1D), (1E), (1F), (1G), (1H), (1I), (1J), (1K), (1L), (1M), (1N), (1O), (1P), (1Q), (1R), (1S) / (1T)

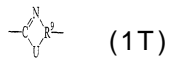
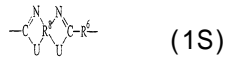


$$0 < x, y < 100\%$$



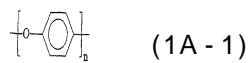
$$0 < y < 100\%$$

- R⁶ - (1P)

$$-R^6-CH=CH-(1Q)$$
$$-\text{CHR}^7 - \text{CH}_2 - (1\text{R})$$


R^6 1,2 - , 1,3 - , 1,4 - , 4,4' - ,
 2가 , C_{10} 2가 , C_{14} 2가 / 2가 (pyrene)
 . C_{10} , C_{14} . /
 R^6 - , - , - .
 R^7 , R^8 , R^9 1가, 2가 3가 ,
 U , , , 1 20 ,
 , 가 .

(copolymer) , Victrex((1)) 720 P Astrel() (homopolymer) .
 , , , , , , , , , , : , , , , , , , , , ,



•

•

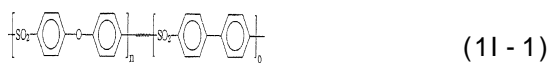


•

Victrex() 200 P

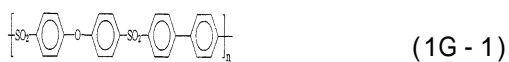


Victrex() 720 P



$n > 0$

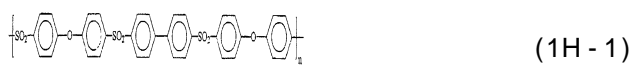
Radel()



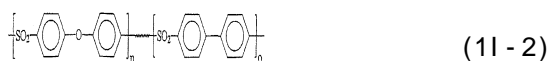
Radel() R



Victrex() HTA



Astrel()



$n < 0$

Udel()

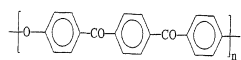


:

PEK

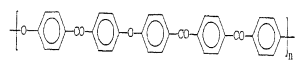


PEKK



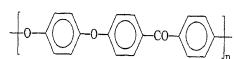
(1K - 1)

PEKEKK



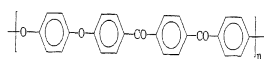
(1L - 1)

PEEK



(1M - 1)

PEEKK



(1N - 1)

:



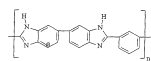
(1P - 1)

:



(1P - 2)

:



(1S - 1)

:

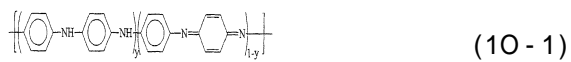


(1P - 3)

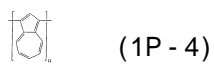
:



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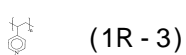
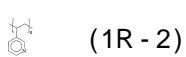
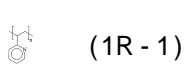
:



:



:



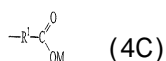
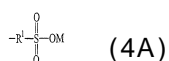
(1A - 1), (1B - 1), (1C - 1), (1I - 1), (1G - 1), (1E - 1), (1H - 1), (1I - 2), (1F - 1), (1J - 1), (1K - 1),
(1L - 1), (1M - 1) / (1N - 1) 가 .

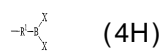
, n
(1) 10 , 100
(1A), (1B), (1C), (1D), (1E), (1F), (1G), (1H), (1I),
(1J), (1K), (1L), (1M), (1N), (1O), (1P), (1Q), (1R), (1S) / (1T) 10 ,
100 .

25,000 g/mol , 50,00
0 g/mol , 100,000 g/mol .

,
(1A), (1B), (1C), (1D), (1E), (1F), (1G), (1H), (1I), (1J), (1K), (1L), (1M), (1N), (1O), (1P), (1Q), (1R), (1S) / (1T)

, R (4A), (4B), (4C), (4D), (4E), (4F), (4G) /
(4H), (4A), (4B), (4C) / (4D), (4A), (4B) / (4C),
(4A):





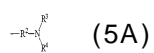
R¹ 1 40 ,

, R¹

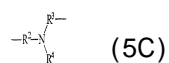
M , , Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, ,
Li⁺,

X .

, , R (5A) / (5B), (5A)
/

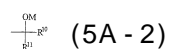
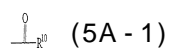


R (5C) / (5D), (5C) .



, R², R³, R⁴ R⁵ 1 40 , R², R³, R⁴

R (5A - 1) / (5A - 2) ,



R^{10} R^{10} , R^{11} R^{10}

(5A - 1)

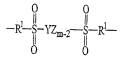
 R^{10} , R^{11}

(5A - 2)

가

R

(6)



(6)

R

, Y 1

40

, 1

6

Z



(7)

H, C, O, N, S, P

20 g/mol

m 2

2

(doping agent)가

(proton conductivity)

가

(dopant)

가

(Cr, Mo, V, W

)

(As, I, P, Se, Si, Te가

)

12 -

(12 - molybdato phosphoric acid) 12 -

(12 - tungstophosphoric acid)

가

 (H_3PO_4)

(degree of doping)

가 가

, 3 15

, 6 12

가

0.5 - 96

1 - 72

100

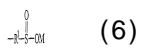
, 0.5 meq/g 1.9 meq/g .

25 100 cm , 50 cm , 20 cm

100 , 120 , 80 ,
가 . 50 100 μ m, 10 90 μ m, 20
80 μ m .

, 90 100% .

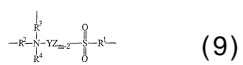
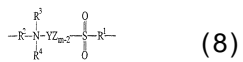
, a), b) d) , d) (6) , 가
(7)



YLm (7)

L , F, Cl, Br, I, , n 2 , 2 .
(1)

(5C) , (7) R (5A) ,
(8) / (9)



(5A) / (5C) 가

1) a) ,

2) b) ,

3) d) .

1) a) b)

2) d)

1) a) d)

2) b)

, 1) a)

2) b) d)

, a), b) d)

(1) 가

(1A), (1B), (1C), (1D), (1E), (1F), (1G), (1H), (1I), (1J), (1K), (1L), (1M), (1N), (1O), (1P), (1Q), (1R), (1S) / (1T)

(1A), (1B), (1C), (1D), (1E), (1F), (1G), (1H), (1I), (1J), (1K), (1L), (1M), (1N), (1O), (1P), (1Q), (1R), (1S) / (1T) 10 , 100

25,000 g/mol,

50,000 g/mol, 100,000 g/mol

a), b) / d)

(aprotic solvent),

(1) (THF)

, n -

L - (10) ()

/

SO₃

SO₂

ui, S. Reichle,

) PSU Udel(

1 (

)" J. Polym. Sci.:

A: Polym. Chem. 34, 2421 - 2438 (1996), WO 00/09588 A

).

4,833,219 (J. Kerres, W. C

), "

- -

(

0.1 3 (group) ,

a) 0.2 0.2 2.2 가 , 0.8 2.2 b) 0.8 1.3 d)

가

, N,N - , N,N - , N

- (sulfolane) ,

a) (substrate), ,

b) , 25 / 1000 mbar 가

,

a) 1 ,

b) 가 , 1

, 25 가

, 100 cm , 2 ,

,

tration), (electrodialysis) (pervaporation), (膜抽出, perstraction), (nanofil 가 (diffusion dialysis)

, 가

, 가

(IEC) , 1mg

50ml NaCl , H⁺ 가 ,

24 , 0.1 - NaOH

IEC

IEC(meq/g) = {NaOH (meq/g) * NaOH (ml) * NaOH (factor)} / (g)

(R^{SP}) (0.25cm²) (Plexiglas unit)

(IM6 , Zahner elektrik) ,

가 0 . 0.5N HCl ,

Nafion 117 , Nafion 117/ /Nafion 117

, Nafion 117 , Nafion

25

, 가 ($= m^{\text{SWOLLEN}}$).
($= m^{\text{dry}}$).

$$Q = (m^{\text{SWOLLEN}} - m^{\text{dry}}) / m^{\text{dry}}$$

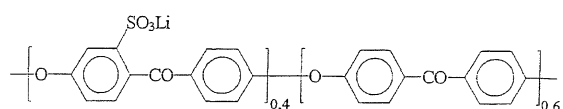
a)

a - 1) PSU Udel()

PSU P 1800 (Amoco)

a - 2) PEK - SO₃ Li:

PEK;

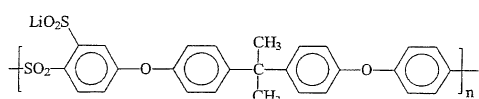


:

0ml 24 1.8 meq SO₃ H/g PEK - SO₃ H 100g 10 % LiOH 100
Li PEK - SO₃ Li ,
, 100 48 0.4 SO₃ Li
{ (IEC) = 1.8 meq SO₃ H/g .

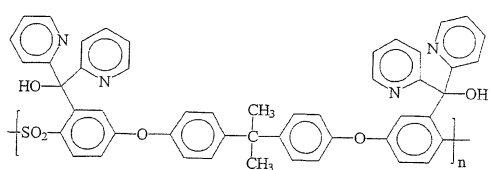
a - 3) PSU - SO₂ Li:

PSU Udel()



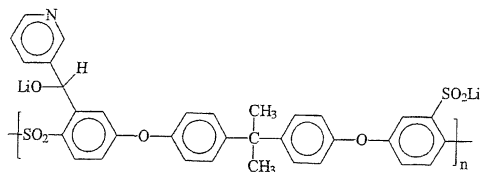
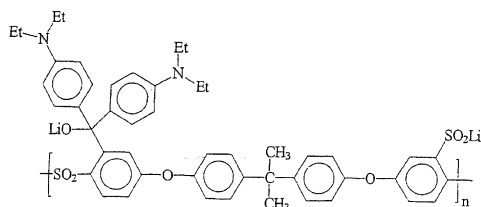
4,833,219 (J. Kerres, W. Cui, S. Reichle,), J. Po
lym. Sci.: A: Polym. Chem. 34, 2421 - 2438 (1996) " - -
() PSU Udel()" , 가 IEC = 1.95 meq SO₂ Li/g .

a - 4) PSU - DPK



2,2' - PSU Udel (WO 00/09588 A1), 2,2' -

a - 5) PSU - P3 - SO₂ Li, PSU - EBD - SO₂ Li

PSU - P3 - SO₂ LiPSU - EBD - SO₂ Li

PSU Udel() THF -75
2.5M n- (n-BuLi)
uLi (batch)
, -3-
-20 가 SO₂ 4,4'-(N,N-
-75 SO₂가 가
, 10ml / 가
, 80
1H-NMR 가

[1] PSU - P3 - S0

| | | |
|--------------------------------|---|---|
| | (BATCH) | |
| PSU - P3 - SO ₂ Li | 10ml 10M BuLi1000ml THF22.1g PSU Udel()5.35g - 3 - SO ₂ | 0.8 - 3 - 1.2 SO ₂ Li |
| PSU - EBD - SO ₂ Li | 10ml 10M BuLi1000ml THF22.1g PSU Udel()16.22g 4,4' - - (N,N -) SO ₂ | 0.4 4,4' - (N,N -) 1.6 SO ₂ Li |

b)

PEK - SO₃ Li, PSU - P3 - SO₂ Li, PSU - EBD - SO₂ Li, PSU - DPK / PSU - SO₂ Li가 2 NMP
 1,4 - (1,4 - diiodobutan 60
 e) (doctor blade) 120
 1 , 가 1 90 , 120
 (waterbath) 90
 10% HCl 60

c) 2 3 (IEC^{theo})
 3 ,
 , 90

[2]

| | | (μm) | IEC ^{exp} (meq/g) | IEC ^{theo} (meq/g) | R ^{sp} (cm) |
|----------|--|-------------------|----------------------------|-----------------------------|----------------------|
| 1(wz054) | 0.77g PSU - EBP2.0g PEK - SO ₃ Li0.6g 1,4 - | 64 | 1.03 | 1.09 | 6.87 |
| 2(wz051) | 0.77g PSU - Pe2.0g PEK - SO ₃ Li0.48g 1,4 - | 87 | 0.81 | 0.88 | 3.62 |
| 3(wz40) | 3g PEK - SO ₃ Li0.3g PSUSO ₂ Li0.3g PSU - DPK0.205ml 1,4 - | 113 | 1.43 | 1.4 | 13.4 |
| 4(wz40R) | 1g PEK - SO ₃ Li0.3g PSUSO ₂ Li0.3g PSU - DPK0.205ml 1,4 - | 52 | 0.86 | 0.89 | 35.96 |
| 1(wz43) | 3g PEK - SO ₃ Li0.3g PSU - DPK | 126 | 1.52 | 1.52 | 7.8 |
| 2(wz43R) | 1g PEK - SO ₃ Li0.5g PSU - DPK | 56 | 0.92 | 0.79 | 24.5 |
| 3 | PEK - SO ₃ H | 82 | 1.63 | 1.8 | 7.13 |

IEC^{exp} :R^{sp} :

[3]

| | (%) | | | |
|--------------------------|--------|-------|--------|--------|
| | 25 | 40 | 60 | 90 |
| 1(wz054) | 40.79 | 46.05 | 46.05 | 59.21 |
| 2(wz051) | 38.46 | 44.61 | 44.61 | 61.54 |
| 3(wz40) | 42 | 42.48 | 58.41 | 151.33 |
| 4(wz40R) | 22.9 | 27.1 | 29.2 | 35.9 |
| 1(wz43) | 95.9 | 110.4 | 161.09 | 224.43 |
| 2(wz43R) | 29 | 33.77 | 34.2 | 48.05 |
| 3PEK - SO ₃ H | 107.32 | 122 | 129.27 | 139.02 |

가

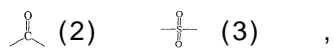
25 100 cm
 (swelling property)

(57)

1.

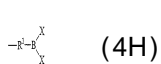
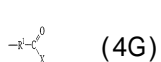
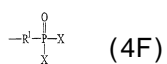
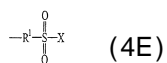
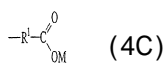
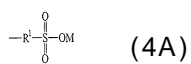
- Q - R (1)

,

[illegible]

R 27a ,

a) R (4A), (4B), (4C), (4D), (4E), (4F), (4G) / (4H)



R¹

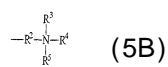
1

40

M, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺,

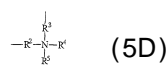
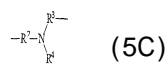
X

b) R (5A) / (5B),

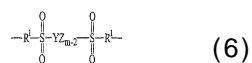
R², R³, R⁴ R⁵

1

40

, R², R³, R⁴ / R (5C) / (5D)

c) R (6) (bridge),



R

Y 1 40

Z



, H, C, O, N, S, P,

, 20 g/

m 2

2.

1, (1) (1A), (1B), (1C), (1D), (1E), (1F), (1G), (1H), (1I), (1J), (1K), (1L), (1M), (1N), (1O), (1P), (1Q), (1R), (1S) / (1T),

- O - R⁶ - (1A)

- S - R⁶ - (1B)

- O - R⁶ - SO₂ - R⁶ - (1C)

- O - R⁶ - SO₂ - R⁶ - O - R⁶ - (1D)

- O - R⁶ - SO₂ - R⁶ - O - R⁶ - R⁶ - (1E)

$\text{---O---R}^6\text{---SO}_2\text{---R}^6\text{---O---R}^6\text{---}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{---R}^6\text{---}$ (1F)

- O - R⁶ - SO₂ - R⁶ - R⁶ - SO₂ - R⁶ (1G)

- O - R⁶ - SO₂ - R⁶ - R⁶ - SO₂ - R⁶ - O - R⁶ - SO₂ - R⁶ - (1H)

$\left[\text{O---R}^6\text{---SO}_2\text{---R}^6 \right]_x \left[\text{SO}_2\text{---R}^6\text{---R}^6 \right]_y$ (1I)

0 < x, y < 100%

- O - R⁶ - CO - R⁶ - (1J)

- O - R⁶ - CO - R⁶ - CO - R⁶ - (1K)

- O - R⁶ - CO - R⁶ - O - R⁶ - CO - R⁶ - CO - R⁶ (1L)

- O - R⁶ - O - R⁶ - CO - R⁶ - (1M)

- O - R⁶ - O - R⁶ - CO - R⁶ - CO - R⁶ - (1N)

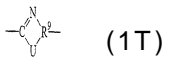
$\left(\text{R---NH---R---NH} \right)_y \left(\text{R---N}=\text{C}_6\text{H}_4=\text{N---R} \right)_{100\%-y}$ (1O)

0 < y < 100%

- R⁶ - (1P)

- R⁶ - CH=CH - (1Q)

- CHR⁷ - CH₂ - (1R)



2가, C₁₀, R⁶, 2가, C₁₄, 1,2 -, 1,3 -, 1,4 -, 4,4' - (pyrene),
 ,
 R⁷, R⁸, R⁹, 1가, 2가, 3가,
 U, , 1, 2,
 0, , 가

3.

1, 2, , , .

4.

1, 3, 25, 100 cm,
 , .

5.

1, 4, 가 90, 100%,
 , .

6.

1, 5, 0.5 meq/g 1.
 9 meq/g, .

7.

1, 6, ,

a), b) d) 가 (7)
 ,

a) b) 1 ,

d) (6) ,

 (6)

YLm (7)

L , n 2 , .

8.

7 ,

1) a) ,

2) b) ,

3) d) 가 , .

9.

7 ,

1) a) b) ,

2) d) 가 , .

10.

7 ,

1) a) d) ,

2) b) 가 , .

11.

7 ,

1) a) ,

2) b) d) 가 , .

12.

7 , a), b) d) 가 , .

13.

7 12 , , N,N - , N,N - (sulfolane) , , .

14.

13 ,

a) (substrate) ,

b) , 25 / 1000 mbar 가

15.

7 14 ,

a) 1 ,

b) 가 ,

1 , .

16.

7 15 , , .

17.

1 6 ,

2 , , .

18.

1 6 ,

(nanofiltration), (electrodialysis) (pervaporation), (膜抽出, perstraction), (diffusion dialysis) , .