Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2014

Cite this: DOI: 10.1039/c0xx00000x
www.rsc.org/xxxxxx
ARTICLE TYPE

Electronic Supplementary Information

Chemicals

Two kinds of commercial anion exchange membranes (AEMs), including homogeneous AEM (Beijing Ting Run Co., China) and heterogeneous AEM (Shanghai Shanghua Water Treatment Material Co., China), were used in this study, both of which contain quaternary ammonium groups ($–N^+(CH_3)_3$) as fixed charge groups. The main characteristic parameters of both of AEMs were given in Table S1. Scanning electron microscopy (SEM) images of a portion of two AEMs used for the electrochemical study were shown in Fig. S1 which were performed using a Hitachi S-3400N (Hitachi, Japan). 1,2-Dichloroethane (DCE), potassium chloride (KCl), lithium chloride (LiCl), magnesium chloride ($MgCl_2$), lithium sulfate (Li_2SO_4), sodium perchlorate ($NaClO_4$), sodium nitrite ($NaNO_2$), potassium nitrate (KNO_3), potassium acetate (KAc), sodium fluoride (NaF), sodium hydroxide (NaOH), tetramethylammonium chloride (TMACl), and tetraethylammonium chloride (TEACl) were obtained from Sinopharm Chemical Reagent Co. and were all analytical grade. Tetrabutylammonium chloride (TBACl, 95%) and sodium tetraphenylborate (NaTPB, 99%) were purchased from J&K. Bis(triphenylphosphoranylidene)ammonium chloride (BTPPACl, 97%) and potassium tetrakis(4-chlorophenyl)borate (KTPBCl, 98%) were supplied by Aldrich and TCI respectively. Tetrabutylammonium tetraphenylborate (TBATPB), bis(triphenylphosphoranylidene)ammonium tetraphenylborate (BTPPATPB), and tetrabutylammonium tetrakis(4-chlorophenyl)borate (TBATPBCl) were synthesized according to the procedure reported elsewhere and used as organic background electrolytes.[3c] Distilled water was employed for preparation of aqueous solutions.

Table S1 Main characteristic parameters of two kinds of commercial anion exchange membranes.[a]

Product code	Type	Fixed groups	Thickness (mm)	Ion-exchange capacity (mol kg^{-1} dry)	Water content (%)	Transfer number	Resistance (Ω cm^2)
JAM-Ⅱ-05	Homogeneous	$–N^+(CH_3)_3$	0.16	1.8-2.2	24-30	0.95	4-8
PE3362	Heterogeneous	$–N^+(CH_3)_3$	0.42	1.8	30-45	0.89	12

[a] The date of two kinds of AEMs from the products specifications.

Apparatus

The contact angles between water or DCE and homogeneous AEM(JAM-Ⅱ-05) were measured using JC2000D1 (Shanghai zhongchen digital technic apparatus co., China). The AEMs were generally saved in the aqueous solution until use. Before the voltammetric experimentation, the water attached to the surface of the AEMs should be wiped out using filter paper. The cut AEM with diameter of 9 mm was attached to a glass tube (outer diameter ~ 9 mm and inner diameter ~ 7 mm) with cyanoacrylate glue (Deli Co., China). The glass tube was then left in contact with the cut AEM about ten minutes for the solidification of glue before being immersed in the organic phase. This process was similar to the arrangement of zeolite membrane modified L/L interface.[4c-e] Insufficient time for the solidification of glue could cause leakage of aqueous solution from the glass tube, which resulted in the overflow of current response (over milliampere-level). The AEM-modified water/1,2-dichloroethane (W/DCE) interface was polarized using a four-electrode potentiostats (CHI660D, CH Instruments. Inc., USA). The homemade four-electrode electrochemical cell was similar to those previous reports,[4l] where a pair of Ag/AgCl electrodes (one in each phase) work as reference electrodes controlling the potential and a pair of Pt-wire electrodes (one in each phase) act as counter electrodes measuring the current. The working electrode is just the membrane-supported liquid/liquid interface. All the experiments were carried out at room temperature (25±3℃).

All the cell setups employed for voltammetric ion transfer studies can be shown as below:

Cell 1: Ag | AgCl | 1 mM TBACl + 12 mM KCl | 20 mM TBATPB (DCE) || x mM R + 100 mM KCl (W) | AgCl | Ag
Cell 2: Ag | AgCl | 1 mM BTPPACl + 12 mM KCl | 20 mM BTPPATPB (DCE) || 100 mM KCl (W) | AgCl | Ag
Cell 3: Ag | AgCl | 1 mM TBACl + 12 mM KCl | 20 mM TBATPBCl (DCE) || 100 mM KCl (W) | AgCl | Ag
Cell 4: Ag | AgCl | 1 mM TBACl + 12 mM KCl | 20 mM TBATPB (DCE) || 100 mM LiCl (W) | AgCl | Ag
Cell 5: Ag | AgCl | 1 mM TBACl + 12 mM KCl | 20 mM TBATPB (DCE) || 50 mM $MgCl_2$ (W) | AgCl | Ag

Where R denotes Li_2SO_4, $NaNO_2$, $NaClO_4$, KNO_3, KAc, NaF, NaOH, TEACl. and TMACl. The double bar in Cell 1 denotes the bare, and the homogeneous or heterogeneous AEM-modified-W/DCE interface. The double bars in Cell 2-5 denote the homogeneous AEM modified W/DCE interface.

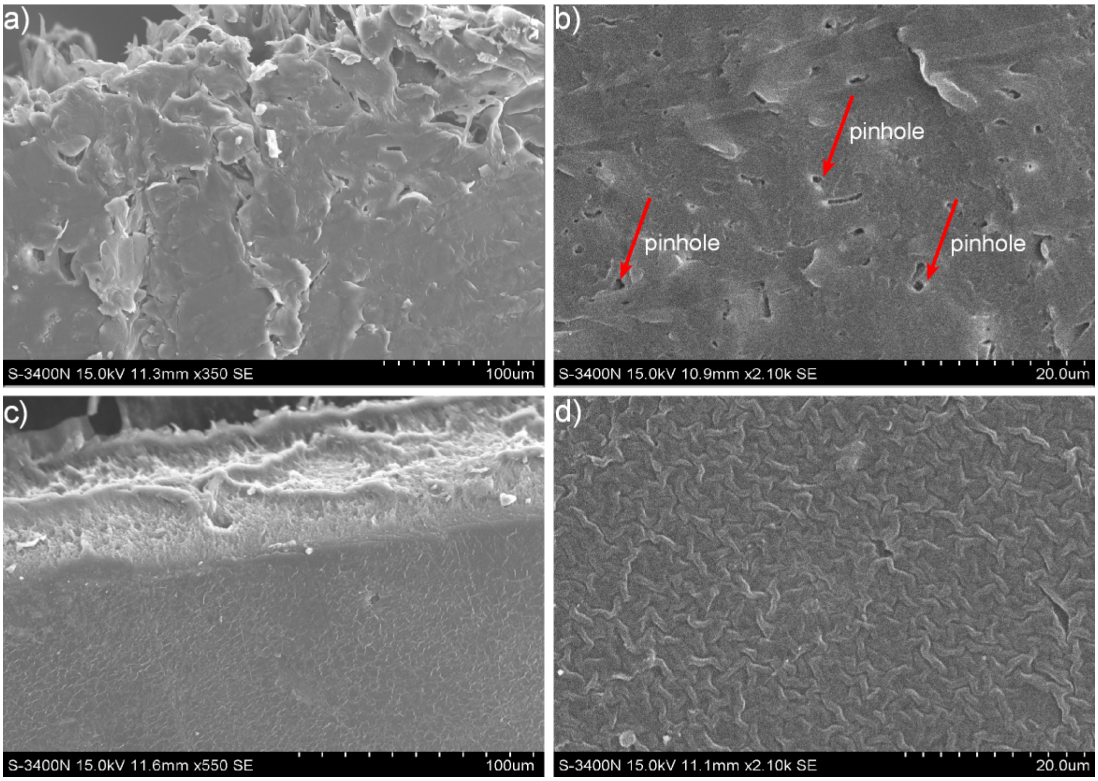


Fig.S1 SEM images of (a, b) heterogeneous (PE3362) and (c, d) homogeneous (JAM-Ⅱ-05) anion exchange membranes employed herein to modify water/1,2-dichloroethane interface.

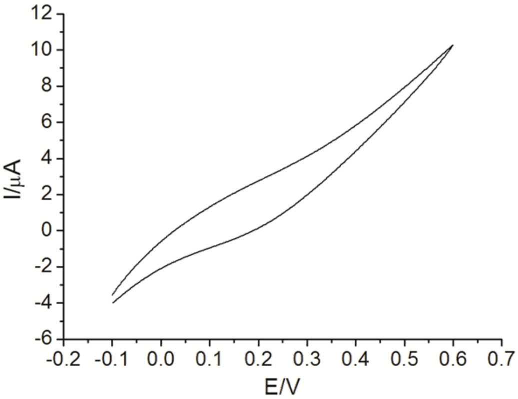


Fig.S2 Cyclic voltammogram for the back ground response (x = 0 in cell 1) in the presence of heterogeneous anion exchange membrane (PE3362) at the W/DCE interface. The scan rate was 50 mV s^{-1}.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

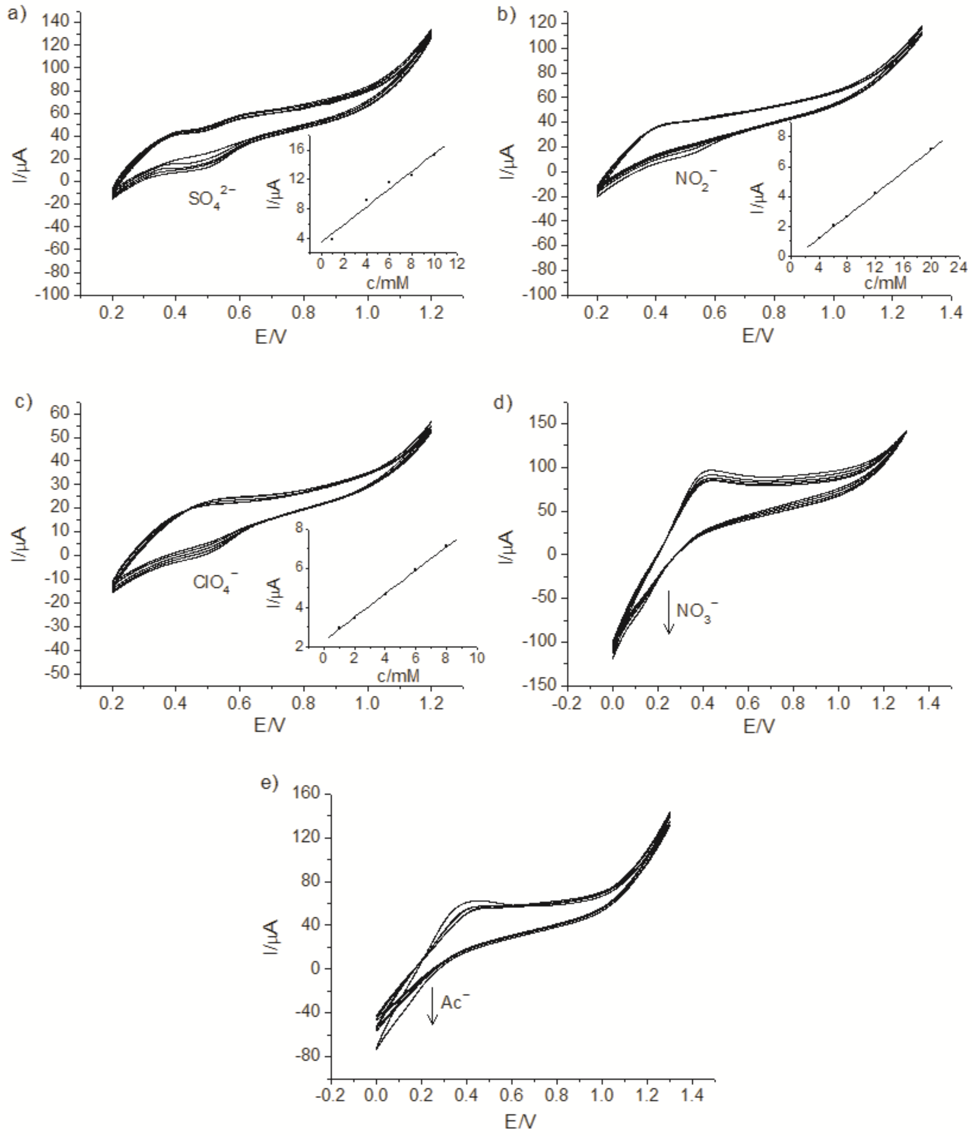


Fig.S3 Cyclic voltammograms of ITs of SO_4^{2-} (a), NO_2^- (b), ClO_4^- (c), NO_3^- (d), and Ac^- (e) at the homo-AEM-modified W/DCE interface using cell 1 with (a) x = 2, 4, 6, 8, and 10 for SO_4^{2-}; (b) x = 4, 6, 8, 12, and 20 for NO_2^-; (c) x = 1, 2, 4, 6, and 8 for ClO_4^-; (d) x = 22, 32, 42, 52, and 62 for NO_3^-; and (e) x = 20, 30, 40, 50, and 60 for Ac^- from top to bottom. The scan rate was 50 mV s^{-1}.

Table S2 (a)The diameters and thermodynamic date of investigated cations.

	TBA^+	$BTPPA^+$	K^+	Li^+	Mg^{2+}	TEA^+	TMA^+
Hydrated diameter (nm)	0.826[a]	1.1×0.74[b]	0.424[c]	0.482[c]	0.598[c]	0.690[c]	0.588[c]
$\Delta_o^w \phi^0$ [V]	-0.276[d]	–	0.50[d]	0.56[d]	–	0.019[d]	0.16[e]
$\Delta G^{o,w\to o}$ [kJ/mol]	-26.6[d]	–	48[d]	54[d]	–	1.8[d]	15.4[e]

[a] Date were bare ion diameter from ref S1. [b] Datum was bare ion diameter from ref. 4d. [c] Date were from ref 11. [d] Date were from ref 3f. [e] Date were from ref S2.

Cite this: DOI: 10.1039/c0xx00000x

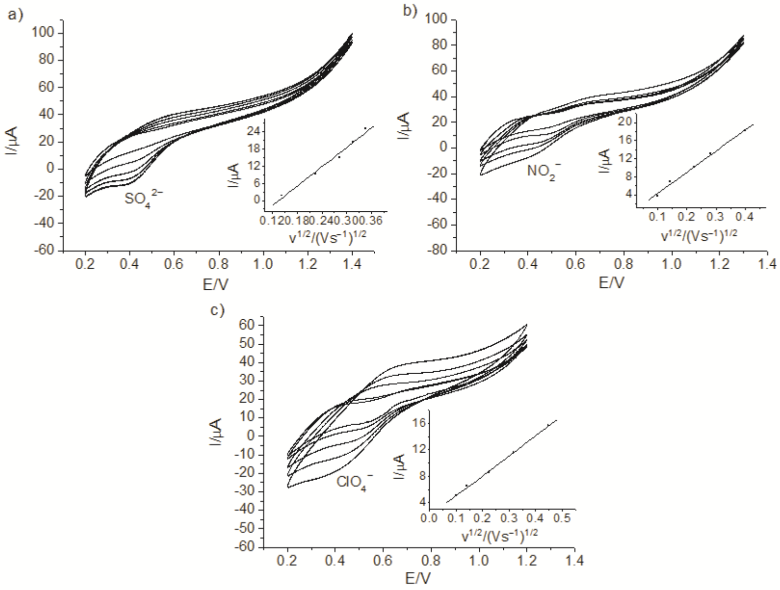
www.rsc.org/xxxxxx

ARTICLE TYPE

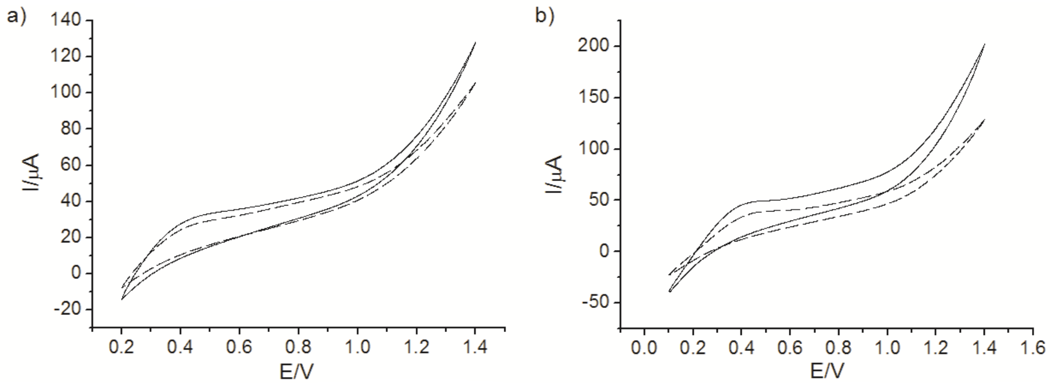
(b) The diameters and thermodynamic date of investigated anions.

	TPB$^-$	TPBCl$^-$	Cl$^-$	SO$_4^{2-}$	NO$_2^-$	ClO$_4^-$	NO$_3^-$	Ac$^-$
Hydrated diameter (nm)	0.842[a]	1.204[f]	0.448[c]	0.546[c]	0.458[c]	0.538[c]	0.446[c]	0.434[c]
$\Delta_o^w\phi^0$ [V]	–	–	-0.52[d]	–	-0.334[d]	-0.17[d]	-0.28[d]	–
$\Delta G^{o,w\to o}$ [kJ/mol]	-35.2[e]	–	50[d]	–	32[d]	16.4[d]	27[d]	–
Ep $^{w\to o}$ [V]	–	–	–	0.47	0.45	0.42	0.13	0.08

[f] Assumed datum approximately from the sum of the diameter of TPB$^-$ and Cl$^-$.



5 **Fig.S4** Cyclic voltammograms of ITs of SO$_4^{2-}$ (a), NO$_2^-$ (b), and ClO$_4^-$ (c) at the homo-AEM-modified W/DCE interface using cell 1 with (a) x = 10 at scan rates of 20, 50, 80, 100, and 120 mV s^{-1}; (b) x = 20 at scan rates of 20, 50, 80, 100, and 120 mV s^{-1}; and (c) x = 10 at scan rates of 10, 20, 50, 100, and 200 mV s^{-1} from top to bottom. Inset: polt of the peak currents against the square root of scan rate.



10 **Fig.S5** Cyclic voltammograms of ITs of TEA$^+$ (a) with x of 10 and TMA$^+$ (b) with x of 10 at the homo-AEM-modified W/DCE interface. The scan rate was 50 mV s^{-1}. The dashed and solid lines correspond to the absence and presence of the cations, respectively.

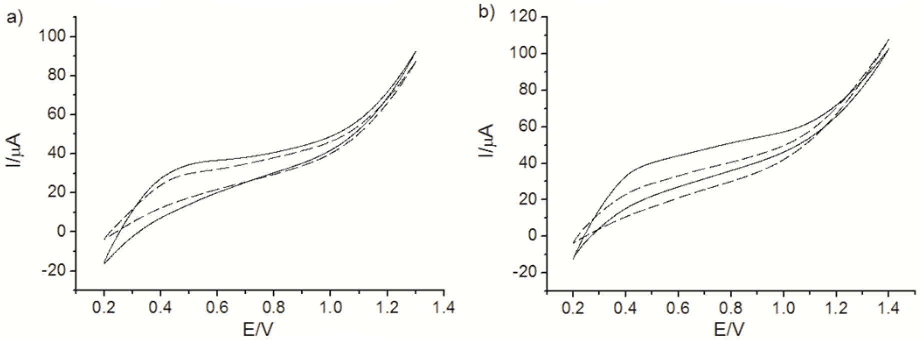


Fig.S6 Cyclic voltammograms of ITs of F^- (a) with x of 10 and OH^- (b) with x of 10 at the homo-AEM-modified W/DCE interfaces. The scan rate was 50 mV s^{-1}. The dashed and solid lines correspond to the absence and presence of the anions, respectively.

S1 T. Osakai and K. Ebina, *J. Phys. Chem. B*, 1998, **102**, 5691-5698.
S2 T. Wandlowski, V. Mareček and Z. Samec, *Electrochim. Acta*, 1990, **35**, 1173-1175