JOURNAL OF APPLIED ELECTROCHEMISTRY **27** (1997) 749–755

Application of a solid ion-exchange electrolyte in three-dimensional electrodes

K. VUORILEHTO, A. TAMMINEN

Helsinki University of Technology, Laboratory of Corrosion and Material Chemistry, Vuorimiehentie 2K, FIN-02150 Espoo, Finland

Received 4 April 1996; revised 26 June 1996

A solid ion-exchange electrolyte was used to solve the problem of low ionic conductivity in three-dimensional electrodes. It was found that packed-bed three-dimensional electrodes, mixed with ion-exchange resins, have good ionic conductivity even when the free electrolyte is distilled water. Ionic group, counter-ion, cross-linking and geometry of the ion-exchanger are the most important parameters when selecting the optimum ion-exchange electrolyte. In most applications, a combination of a strong cation exchanger, small monovalent counter-ions, a low degree of cross-linking and a small particle size gives good ionic conductivity for the three-dimensional electrode.

1. Introduction

Three-dimensional electrodes are used in electrochemical systems where a high electrode area is needed. The most typical application is the electrowinning of metals from waste water, others being, for example, batteries, organic synthesis and electrochemical deoxygenation.

Extensive use of three-dimensional electrodes is hindered by the demand for good conductivity of the electrolyte. The liquid used in an electrochemical cell must contain enough free ions to carry the charge between the electrodes. In three-dimensional electrodes, the ions also have to transport the charge inside the electrodes, and the need for ionic conductivity thus becomes pronounced [1].

In this work, a three-dimensional electrode, which works even in non-conducting liquids, was developed by using ion-exchange resin as a solid electrolyte. The basic idea was to mix the electrode material with ion-exchange resin, in which the ions can migrate (Fig. 1). This eliminates the need for free ions in the liquid, and even pure water can be used in the electrochemical cell.

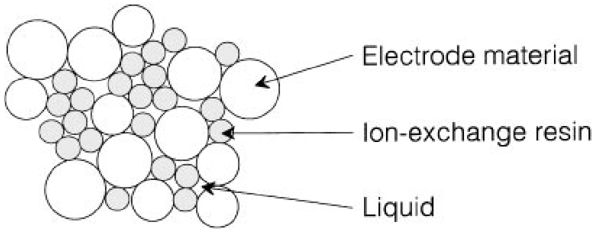

Fig. 1. Ion-exchange resin, used as a solid ion-exchange electrolyte inside a three-dimensional electrode.

2. Brief survey of the solid ion-exchange electrolyte

2.1. *Mechanism of the ionic conductivity*

The ion-exchange electrolyte consists of densely packed ion-exchange particles, surrounded by liquid. In the ion-exchange particles electric charge is carried by counter-ions, in the liquid by free ions. The charge can be transported by three different routes through the bed of solid ion-exchange electrolyte and liquid (Fig. 2): (1) alternating through the liquid and the particles, (2) solely through the particles or (3) through the liquid, avoiding the particles.

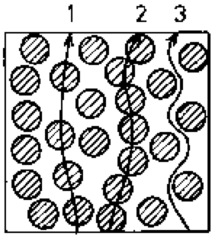

Fig. 2. Schematic picture of the charge transport through a bed of solid ion-exchange electrolyte and liquid [2].

In most cases the first mechanism predominates. The second mechanism predominates when the conductivity of the liquid is very low. If the conductivity of the liquid is considerably higher than that of the particles, the third mechanism becomes the most important. In this case there is no reason to use an ion-exchange electrolyte.

An example of the conductivity of the bed as a function of the conductivity of the liquid [2] is shown in Fig. 3. The left endpoint of the curve corresponds to the situation where the charge is transported solely along the ion-exchange particles. At the point where the conductivity of the bed is equal to the conductivity of the liquid, the ion-exchange material has the same conductivity as the liquid. Thus, based on this equiconductance point the specific conductivity of the ion exchange material can be measured.

0021-891X © 1997 Chapman & Hall

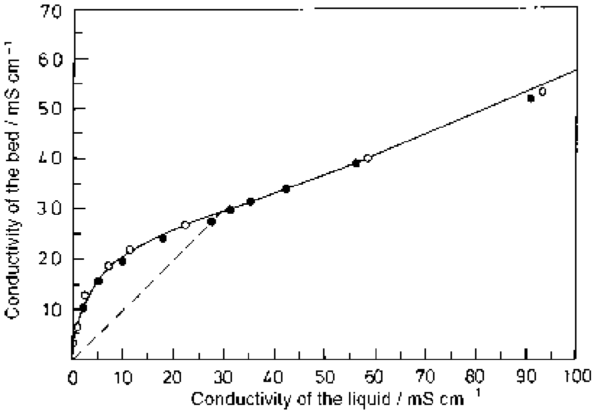

Fig. 3. The conductivity of an ion-exchanger bed as a function of the conductivity of the liquid. (Dowex 50X8 (○) or Amberlite IR-120 (•), in aqueous NaCl-solution) [2].

2.2. *Structure of ion-exchange resins*

Ion-exchange resin is typically produced in the form of small spheres (diameter 0.1–1.5 mm), consisting of a net-like polymer (Fig. 4). The most common polymer used is polystyrene, which contains a few per cent of divinylbenzene (DVB) as a cross-linking agent. An ionic group, which is able to bind counter-ions by its charge, is attached to each benzene ring.

The ion-exchangers are divided into four categories based on the ionic groups [4]: in strongly acidic cation exchangers the ionic group is typically a sulfonic acid group, $-SO_3^-$, and in weakly acidic cation exchangers a carboxylic acid group, $-COO^-$. In strongly basic anion exchangers the ionic group is a quaternary ammonium group, in weakly basic anion exchangers a tertiary or secondary amino group.

2.3. *Conductivity of ion-exchange resins*

In the ion-exchange particles, the charge is carried by counter-ions that move inside the resin (Fig. 4). As ionic groups are immobile and there are very few co-ions, the conductivity of the ion-exchange resin only depends on the concentration and mobility of counter-ions.

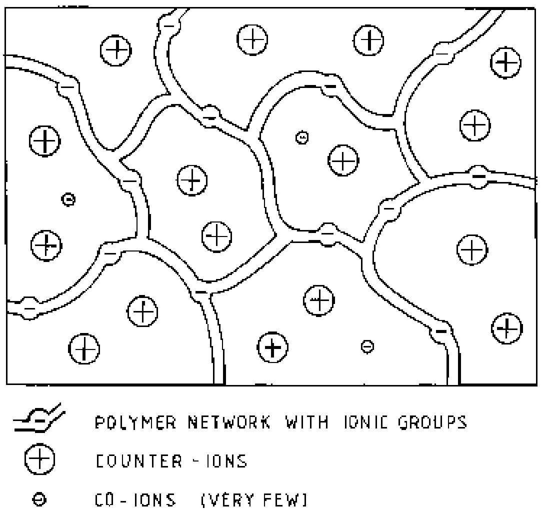

Fig. 4. The net-like structure of the ion-exchange resin [3].

The concentration of counter-ions in an ion-exchange resin is high, typically 1–2 mol dm^{-3} (for bivalent ions, half this amount). This concentration equals the concentration of ionic groups, and is almost independent of the liquid surrounding the ion-exchanger.

The mobility of ions inside the ion-exchange resin is much lower than in an aqueous solution because of the friction caused by the network and the electrostatic attraction of the fixed ionic groups [3].

When an ion-exchange resin is used as an electrolyte, the conductivity is of major importance. It can be optimized by: (i) using small ions, e.g. K^+ or F^-; (ii) using monovalent ions. The mobility of monovalent cations in the resin is 1/4 – 1/3 of their mobility in water. For bivalent cations this number is about 1/8 [5]; (iii) using resin that has a coarse network. This is achieved by reducing the amount of divinylbenzene in the polymer structure; and (iv) using a high temperature. An elevated temperature increases the mobility of ions in the resin even more than it increases the mobility of ions in water [3].

For example, a strongly acidic cation exchanger in the Na^+-form, with 8% divinylbenzene (Fig. 3), has a conductivity of 30 mS cm^{-1}. This conductivity is equal to that of a 0.3 mol dm^{-3} aqueous NaCl-solution [2].

2.4. *Previous research in the field of solid ion-exchange electrolytes*

The most common ion-exchange electrolytes are the ion-exchange membranes. These are generally used to separate electrode chambers, but in some applications, as in fuel cells and in organic electrosynthesis, they are used explicitly as electrolytes [6]. In these cases, the anode and the cathode are fixed to opposite sides of the membrane, in direct contact with the membrane surface. As the membrane can transport the ions, typically H^+, between the electrodes, no other electrolyte is needed. These two-dimensional solid ion-exchange electrolytes are often called ‘solid polymer electrolytes’.

The conductivity of three-dimensional ion-exchanger beds has been studied mostly for academic reasons [7]. One practical aim has been the development of ion-exchange columns that are regenerated electrochemically. During regeneration, the H^+-ions generated by the anode and the OH^--ions generated by the cathode, replace the foreign ions in the ion-exchanger [3]. In another possible application, the ion-exchanger has been used to increase the mobility of ions, when treating dilute aqueous solutions in an electrochemical cell [8]. In all cases the electrodes have been two-dimensional.

Table 1. Ion-exchange resins

Resin type and name	*Structure*	*Diameter*
Strongly acidic cation exchangers:		
Amberlite 200*	styrene–20% DVB	0.3–1.2mm
Amberlite IR-120*	styrene–8% DVB	0.3–1.2mm
Dowex 50X8†	styrene–8% DVB	0.4–1.2mm 0.15–0.3mm 0.075–0.15mm
Dowex 50X4†	styrene–4% DVB	0.15–0.3mm
Dowex 50X2†	styrene–2% DVB	0.15–0.3mm
Smopex-101‡	polypropene + styrene	fibrous, length 4mm, diam. 40 μm
Weakly acidic cation exchanger:		
Dowex CCR-2†	acrylic acid	0.3–0.84mm
Strongly basic anion exchanger:		
Amberlite IRA-400*	styrene–4% DVB	0.3–1.2mm
Weakly basic anion exchanger:		
Amberlite IRA-68*	acrylic acid	0.3–1.2mm

* Amberlite is a trademark of Rohm & Haas
† Dowex is a trademark of Dow Chemical
‡ Smopex is a trademark of SmopTech

3. Experimental details

3.1. *Ion-exchange resins*

Nine types of ion-exchange resins were investigated (Table 1). All resins were commercial products. Before use, they were rinsed and regenerated with the appropriate salt solution.

3.2. *Conductivity measurement*

The ionic conductivities of various ion-exchange electrolytes were measured by a Knick-702 conductivity meter with a four-pole measuring electrode. In the four-pole electrode the current flowed between the outer poles, and the potential drop was measured between the two inner poles. The resistance in the electrode/resin interface was so high that potential could not be measured using the current feeder poles.

For measurements, two flow cells were made of acrylic plastic. The first was filled with ion-exchange resin and liquid, the second only with liquid (Fig. 5). The upper surface of the ion-exchanger bed was kept free during the experiments to prevent compaction pressure. The flow was used solely to change the liquid; during measurements there was no flow.

Conductivity meters and measuring cells, such as the Knick-702, use alternating current, but almost all electrochemical cells use direct current. To solve this problem, a d.c.-conductivity meter was also built. This was composed of two platinum electrodes, which were used as current feeders and of two calomel reference

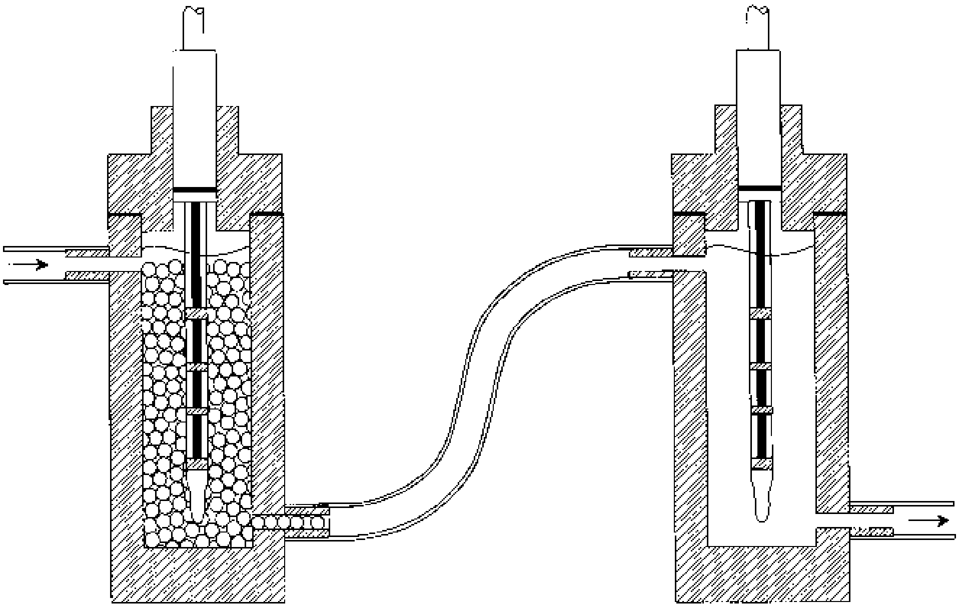

Fig. 5. Experimental setup to measure the ionic conductivity of the ion-exchange electrolyte and the liquid.

electrodes located between them to measure the potential drop. The results obtained with this meter were consistent with those obtained with the Knick-702 and are, therefore, not reported separately.

In all experiments, the conductivity of the ion-exchange electrolyte was measured as a function of the conductivity of the liquid. The experiments were started using a concentrated aqueous solution (100–400 mS cm^{-1}). The solution was then stepwise diluted with distilled water until its conductivity was lower than 0.004 mS cm^{-1}. In the cation exchangers the counter-ions were H^+, Na^+ or Ca^{2+}, and the liquid between the particles was an aqueous solution of HCl, NaCl or $CaCl_2$, respectively. In the anion exchangers the counter-ions were OH^-, Cl^- or SO_4^{2-}, and the solutions NaOH, NaCl or Na_2SO_4. The temperature was kept at 25 °C.

4. Results

The influence of the ionic group, the counter-ion, the cross-linking and the particle geometry, on the conductivity of the ion-exchange electrolyte was studied. Finally, the conductivity of the ion-exchange electrolyte inside a three-dimensional electrode was investigated.

4.1. *Influence of the ionic group and the counter-ion of the ion-exchanger*

In the first stage strongly acidic (SO_3^-group), weakly acidic (COO^-), strongly basic (quaternary ammonium) and weakly basic (tertiary amino) ion-exchangers were compared with each other. Simultaneously the influence of the counter-ion species was studied.

From each category, a typical ion-exchange resin was selected. Examples of the resulting conductivity curves are shown in Fig. 6.

Three parameters were chosen for the comparison of ion-exchange resins: (a) the conductivity of the bed when it equalled the conductivity of the liquid. This is the specific conductivity of the ion-exchanger material; (b) the conductivity of the bed when the conductivity of the liquid was 0.2 mS cm^{-1}. This is of practical importance, as the conductivities of tap-water are typically of this order; and (c) the conductivity of the bed when the conductivity of the liquid approached zero. This figure characterizes the contact between ion-exchanger particles.

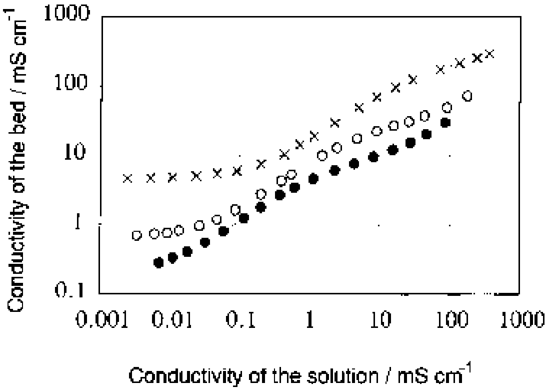

Fig. 6. The conductivity of a strongly acidic cation exchanger bed (Amberlite IR-120) as a function of the conductivity of the solution. The counter-ions were H^+ (×), Na^+ (○) or Ca^{2+} (●).

The results are shown in Table 2. When the specific conductivity (a) of the ion-exchange resin was high, the ion-exchange electrolyte also worked well in liquids of low conductivity (b). When the conductivity of the liquid approached zero the charge was transported solely along the ion-exchanger particles. The conductivity of this kind of ion-exchange electrolyte (c) was about 1–2% of the specific conductivity.

Weak ion-exchangers cannot transport H^+- and OH^--ions. This makes it difficult to use them, as H^+ and OH^- are common products and reactants in electrochemical reactions. During the measurements, a small amount of ions leaked from the weak ion-exchangers. For this reason the values designated – in Table 2 could not be measured.

Table 2. Conductivity of the ion-exchanger bed; various ionic groups and counter-ions

Resin	*Counter-ion*	*Bed conductivity* / mS cm^{-1}		
		(a) *Specific conductivity*	(b) *Solution* 0.20 mS cm^{-1}	(c) *Solution* 0.00 mS cm^{-1}
Strongly acidic (IR-120)	H^+	260	7.4	4.6
	Na^+	33	2.8	0.7
	Ca^{2+}	10	1.8	0.2
Weakly acidic (Dowex CCR-2)	H^+	0.3	0.26	< 0.1
	Na^+	21	2.3	–
	Ca^{2+}	0.12	0.16	< 0.1
Strongly basic (IRA-400)	OH^-	100	2.5	0.6
	Cl^-	27	2.5	0.6
	SO_4^{2-}	20	1.5	0.2
Weakly basic (IRA-68)	OH^-	*	*	*
	Cl^-	35	2.7	–
	SO_4^{2-}	17	1.6	–

* disintegrates

The conductivities of the strongly acidic cation exchangers and the strongly basic anion exchangers were of the same order. The best conductivities were achieved using H^+- and OH^--ions. This phenomenon arises from their ability to jump from one water molecule to another and is not restricted to ion-exchange electrolytes only. The conductivity of the bivalent Ca^{2+}-ion in cation exchangers was rather low. This was also true for SO_4^{2-}-ions in anion exchangers, even if not so pronounced.

Strongly acidic cation exchangers and strongly basic anion exchangers were found to be suitable for use as ion-exchange electrolytes. Cation exchangers were selected for detailed study as they are chemically more stable than anion exchangers.

4.2. *Influence of cross-linking*

Decreasing the amount of divinylbenzene (DVB) in the ion-exchange resin decreases the cross-linking and makes the polymer network coarser. To investigate the influence of cross-linking on conductivity, five strongly acidic cation exchange resins were compared. To exclude the possibility of differences between various manufacturers, two resins of 8% DVB were included. The results are shown in Table 3. Counter-ions and the parameters (a)–(c) are as in Section 4.1.

The lower the content of divinylbenzene in the resin, the higher was the conductivity. This effect was pronounced when the bivalent calcium was used as the counter-ion. The disadvantage in lowering the DVB-content was that the mechanical and chemical stability of the resin was reduced. In distilled water the 2% DVB resin swelled so strongly that the concentration of ions inside the resin decreased, and the conductivity of the resin thus fell. This was why the 2% resin had lower conductivity than the 4% resin in the H^+- and Na^+-forms. In the Ca^{2+}-form, the swelling was moderate, and the conductivity did not fall.

4.3. *Influence of particle geometry*

Ion-exchanger particles are mostly spherical. In order to find the optimum particle size, three sizes of Dowex 50X8 -resin were compared. In addition, a mixture of the largest and the smallest particles was investigated. The conductivities measured are shown in Table 4. Results obtained with the fibrous Smopex-101-resin are included. Smopex-fibres were 4 mm long and 40 μm in diameter.

The particle size had almost no influence on the conductivity of the bed. On the other hand, the size distribution was very significant in solutions of low conductivity. In the large spheres, the ions can move long distances without passing from one sphere to another. However, transitions from one sphere to another cause high resistance as there are only a few contact points between the spheres (Fig. 7). In a bed made of smaller spheres, there are more contact points, but also more transitions. When large and small spheres are mixed, the small ones fill the space between the large ones. This way there are enough contact points and it is still possible to move long distances inside the spheres.

The conductivity of the fibrous Smopex was excellent, especially in distilled water (parameter (c)). The ions can pass more easily from one fibre to another than from one sphere to another because the fibres have numerous crossing points.

The geometry of the contact points is sensitive to the compaction pressure, and typically the contact area increases with increasing pressure. Therefore, a moderate pressure is favourable for the ion-exchange electrolyte. However, a very high pressure can destroy the resin mechanically. For the sake of con-

Table 3. Conductivity of the ion-exchanger bed; various degrees of cross-linking

Resin	*Counter-ion*	*Bed conductivity* / mS cm^{-1}		
		(a) *Specific conductivity*	(b) *Solution* 0.20 mS cm^{-1}	(c) *Solution* 0.00 mS cm^{-1}
20% DVB	H^+	50	2.4	0.4
(Amb-200)	Na^+	8	1.4	0.1
	Ca^{2+}	1.5	0.6	0.03
8% DVB	H^+	260	7.4	4.6
(IR-120)	Na^+	33	2.8	0.68
	Ca^{2+}	10	1.8	0.20
8% DVB	H^+	270	6.4	3.4
(Dowex 50X8)	Na^+	32	2.4	0.57
	Ca^{2+}	8.3	1.5	0.16
4% DVB	H^+	325	7.9	5.0
(Dowex 50X4)	Na^+	47	2.7	0.9
	Ca^{2+}	20	2.1	0.60
2% DVB	H^+	350	6.6	3.9
(Dowex 50X2)	Na^+	51	2.9	0.71
	Ca^{2+}	29	2.7	0.80

Table 4. Conductivity of the ion-exchanger bed; various particle geometries

Resin	*Counter-ion*	*Bed conductivity* / mS cm^{-1}		
		(a) *Specific conductivity*	(b) *Solution* 0.20 mS cm^{-1}	(c) *Solution* 0.00 mS cm^{-1}
0.4–1.2 mm	H^+	270	6.4	3.4
(Dowex 50X8)	Na^+	32	2.4	0.57
	Ca^{2+}	8.3	1.5	0.16
0.15–0.3 mm	H^+	250	7.4	4.7
(Dowex 50X8)	Na^+	30	2.5	0.75
	Ca^{2+}	8.2	1.5	0.17
0.075–0.15 mm	H^+	260	7.7	4.8
(Dowex 50X8)	Na^+	31	2.6	0.70
	Ca^{2+}	10.5	1.7	0.22
0.4–1.2 and	H^+	250	17	12
0.075–0.15 mm	Na^+	30	4.7	1.5
(Dowex 50X8)	Ca^{2+}	8.6	2.7	0.65
40 μm	H^+	340	10	8.7
(Smopex-101)	Na^+	32	2.5	1.6
	Ca^{2+}	16	1.1	0.45

venience, the results reported here were measured without pressure.

4.4. *Influence of the three-dimensional electrode*

When using an ion-exchange electrolyte in a three-dimensional electrode, the electrode material has to be taken into account as a third phase in addition to the resin and the liquid (Fig. 1). The electrode material is not permeable to ions, so it hinders the movement of the ions in the electric field.

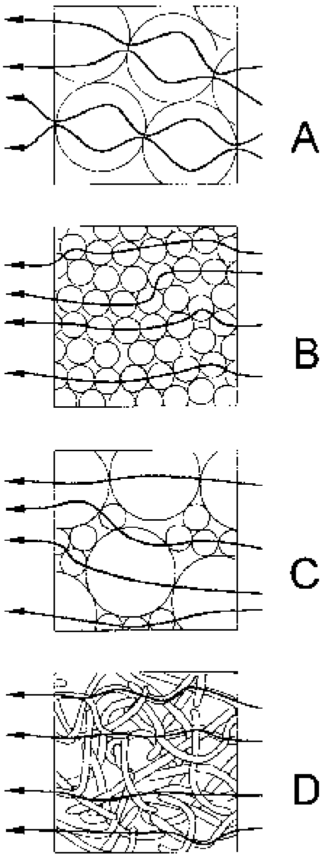

Fig. 7. The influence of the particle geometry on the ion paths. (a) large spheres, (b) small spheres, (c) mixture and (d) fibres.

To estimate the effect of the electrode material, a bed of 50% ion-exchanger particles and 50% glass spheres (diameter 0.5 mm) was mixed. Glass spheres were used instead of real electrode material because the electron-conductivity of the electrode material would have disturbed the measurement of ionic conductivity.

Different kinds of cation exchangers were examined; IR-120 because of its good availability and stability, Dowex 50X4 and 50X2 because of their high conductivity, and Smopex-101 because of its special geometry. The results are shown in Table 5. The specific conductivity (parameter (a)) was not measured as it has no physical meaning due to the glass spheres.

Table 5. Conductivity of the ion-exchange electrolyte inside a three-dimensional electrode

Resin	*Counter-ion*	*Bed conductivity* / mS cm^{-1}	
		(b) *Solution* 0.20 mS cm^{-1}	(c) *Solution* 0.00 mS cm^{-1}
0.3–1.2 mm	H^+	0.9	0.15
Styrene-8% DVB	Na^+	0.43	< 0.1
(IR-120)	Ca^{2+}	0.37	< 0.1
0.15–0.3 mm	H^+	5.3	4.1
Styrene-4% DVB	Na^+	1.5	0.65
(Dowex 50X4)	Ca^{2+}	1.0	0.29
0.15–0.3 mm	H^+	3.8	2.9
Styrene-2% DVB	Na^+	1.1	0.5
(Dowex 50X2)	Ca^{2+}	1.1	0.5
40 μm	H^+	5.5	4.5
Polypropene	Na^+	1.3	0.8
(Smopex-101)	Ca^{2+}	0.65	0.29

The conductivity of the IR-120 resin with glass spheres was poor. This was probably due to the size of the ion-exchanger particles which was of the same order as the size of the glass spheres. The glass spheres were situated between the ion-exchanger particles and thus prevented the ions from passing from one particle to another.

The conductivity of the resins Dowex 50X4 and 50X2 was only slightly lower with glass spheres than without them. The glass spheres occupied some space and disturbed the movement of ions. Still, the small ion-exchanger particles were able to keep good contact with each other by filling the space between the larger glass spheres. In the H^+- and Na^+-forms, the 50X4 -resin had higher conductivity than the 50X2, in Ca^{2+}-form the 50X2 -resin was better.

The thin Smopex-101-fibres fitted easily between the glass spheres, and a reticular ion-exchanger structure took shape. The conductivity was good.

Generally, good conductance was achieved when the geometry of the ion-exchanger particles was such that ions could go round the electrode material by passing from one particle to another.

5. Discussion and conclusions

The solid ion-exchange electrolyte works well in three-dimensional electrodes. When ion-exchange resin is added to the electrode material even liquids of low conductivity can be used in the electrochemical cell.

The main factors influencing the conductivity of the ion-exchange electrolyte are the ionic group and the counter-ion (Table 2), the degree of cross-linking (Table 3) and the geometry of the particles (Tables 4 and 5). A low valency and a small size increase the mobility of the counter-ion. So does a low degree of cross-linking, though it can put the stability of the resin at risk. Particles of small size or fibrous geometry have the best contact with each other and thus facilitate the transport of ions.

The usefulness of the ion-exchange electrolyte in applications of low current density and low conductivity can be illustrated as follows: In a cell, in which the geometric current density is $5\ \mathrm{mA\ cm^{-2}}$ and the allowed potential drop is 0.5 V, the maximum bed depth is 0.5 cm, when using the ion-exchange electrolyte (Dowex 50X4, H^+-form, solution $0.2\ \mathrm{mS\ cm^{-1}}$). In the same cell, without an ion-exchange electrolyte, the maximum depth would be less than 0.01 cm.

The optimum electrode/resin ratio need not be exactly 1:1, but can vary from application to application. If the amount of electrode material is reduced, part of the electrode surface area is lost. In addition, the contact between the electrode particles can be interrupted and the movement of the electrons thus prevented. On the other hand, too small an amount of ion-exchange electrolyte cannot transport ions adequately. The 1:1 -ratio is a good starting point for optimization as it ensures some conductivity for both electrons and ions.

There is no superior ion-exchange resin, but the most suitable resin has to be chosen according to the application: (i) If there are free ions in the liquid, the same species should be used as counter-ions to avoid the replacement of the counter-ions by the free ions. If there are no free ions, H^+ and OH^- are the best counter-ions; (ii) The resin should be weakly cross-linked if this is permitted by the conditions in the cell; and (iii) The particle geometry should be fitted to the electrode geometry so that ions can move along the ion-exchanger particles and electrons can move along electrode particles without interruption.

An ion-exchange electrolyte has been successfully used in electrochemical deoxygeneration of water [9]. Generally, a three-dimensional electrode with a solid ion-exchange electrolyte is a possible choice whenever the liquid has low conductivity and the concentration of reactants is low.

References

[1] F. Goodridge and A. R. Wright, Porous flow-through and fluidized-bed electrodes, *in* 'Comprehensive treatise of electrochemistry' edited by E. Yeager, B. E. Conway, J. O'M. Bockris and S. Sarangapani, vol 6, Plenum Press, New York (1983) pp. 393–443.

[2] K. S. Spiegler, R. L. Yoest and M. R. J. Wyllie, *Disc. Faraday Soc.* **21** (1956) 174.

[3] F. Helfferich, 'Ion Exchange', McGraw-Hill, New York (1962) 621 pp.

[4] K. Dorfner, 'Ion exchangers', Walter de Gruyter, Berlin (1991) pp. 1–187.

[5] A. O. Jakubovic, G. J. Hills and J. A. Kitchener, *Trans. Faraday Soc.* **55** (1959) 1570.

[6] J. Jörissen, *Electrochim.Acta* **41** (1996) 553.

[7] N. P. Gnusin, N. P. Berezina, V. P. Beketova and T. A. Merkulova, *Elektrochimiya* **13** (1977) 1712.

[8] R. L. Sampson and A. H. Sampson, 'Electrolytic process and apparatus for the controlled oxidation or reduction of species in aqueous solutions', *European Patent*. 94 116 808.0. Appl.:25 Oct.1994.

[9] A. Tamminen and K. Vuorilehto, 'Application of a three-dimensional ion-exchange electrolyte in the deoxygenation of low-conductivity water'. To be published.