Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.980977

56 (2015) 3264–3268
December

Electrode overvoltage in low concentrated electrolytes

M. Doležel*, L. Machuča

Membrain s.r.o, Pod Vinicí 87, 471 27, Stráž pod Ralskem, Czech Republic, Tel. +420 727942655;
email: marek.dolezel@membrain.cz (M. Doležel), Tel. +420 602506423; email: lubomir.machuca@membrain.cz (L. Machuča)

Received 28 July 2014; Accepted 7 October 2014

ABSTRACT

Sufficient knowledge about ongoing electrode reactions is necessary for evaluation of electric potential loss in electrode chambers of electrodialysis (ED) modules. Binary electrolytes are usually used as electrode solutions in practice. Kinetic parameters like electrode overvoltage of the gases generation can be described by Tafel's equation. Due to the lack of literature information it was proceeded to testing of chlorides, sulfates, and nitrates of univalent cation salts on electrodes of platinum activated titanium anodes (Pt/ATA). The tests were carried out on a modified ED module with the electrode active area of 64 cm^2 in three-electrode circuit. Exchange current densities and symmetric coefficients of Tafel's equation were calculated from voltage–current data.

Keywords: Overvoltage; Weak concentrated electrolyte

1. Introduction

Electrodialysis (ED) is one of the advanced technologies used for regeneration, desalting or concentrating of solutions (whey, juice, sea and potable water, rinse water) without change of physical state or growing of waste volume. ED uses a selective transport of dissociated ions through Ralex® membrane induced by electrical field. The selective transport is held by acid or alkaline groups bounded in chemical structure of polymer membrane material, which in hydrated state are dissociated and permits reversal exchange of counterions with solution. Electrical field causes electrophoretic effect and ions migrate through membrane from one compartment to the next. ED module with sandwich-ordered anion- and cation-selective membranes allows transport of dissociated salts between module compartments

Drop of electrical potential and loosing of power can be caused by some reasons, e.g. transfer of electrical charge from electrolyte into electrode mass and vice versa. This transfer of electrical current is connected with an electrochemical reaction on the electrode surface. Voltage drop can be described as overvoltage depending on type of the electrode reaction, electrolyte composition, and material of the electrode surface. Overvoltage is defined as difference between electrode potential of electric unloaded electrode—cathode (C) or anode (A) and electrode in working state with given electric current Eqs. (1) and (2). The most common electrode reaction in ED modules is gas evolution—hydrogen Eq. (3), oxygen Eq. (4), and chlorine Eq. (5). Recent scientific literature

---

*Corresponding author.

Presented at the MELPRO 2014 Conference Membrane and Electromembrane Processes,
18–21 May 2014, Prague, Czech Republic

was focused preferably on studying of gas evolution from acid or hydroxide solutions [1–3]. Any works focused on oxygen and hydrogen evolution from the solution of weak concentrated salt, in recent literature, were not found. Roberge [4] was dealing with corrosion kinetics in soil and showed corrosion (exchange) current density i_0 of the hydrogen reaction on the platinized electrode cca 10 mA cm^{-2}. Tseung [3] studied oxygen evolution on electrodes of platinum metal alloys in 1 M H_2SO_4 and 5 M H_2SO_4 shows $i_0 = 4.2\ 10^{-7}$ mA cm^{-2}.

$$\eta_A = E_A(i) - E_A^0 \tag{1}$$

$$\eta_C = E_C(i) - E_C^0 \tag{2}$$

$$\mathrm{H_3O^+ + e^- \rightarrow \frac{1}{2}H_2 + H_2O} \quad E^0 = 0\mathrm{V\ vs.SCE}\ [5] \tag{3}$$

$$\mathrm{3H_2O - 2e^- \rightarrow 2H_3O^+ + \frac{1}{2}O_2} \quad E^0 = 1.229\mathrm{V\ vs.SCE}\ [5] \tag{4}$$

$$\mathrm{2Cl^- - 2e^- \rightarrow Cl_2} \quad E^0 = 1.358\mathrm{V\ vs.SCE}\ [5] \tag{5}$$

H—overvoltage, E_A(i)—potential of current loaded anode, $E_A{}^0$—potential of non-loaded anode.

The dependence of voltage loss by activation overvoltage on current density is non-linear. Activation overvoltage is a function of reduction potential of appropriate reaction described by Butler–Volmer equation Eq. (6). B–V equation is an expression of activation energy of the electrode reaction and appropriate reaction rate described by Bouzek [6]. Knowledge of exchange current density (i_0(C), i_0(A)) and symmetry coefficient (α_C, α_A) is a condition for mathematical modeling and prediction of voltage loss in ED module. Tafel's equation Eq. (8) is arranged by neglecting reverse reaction, and limiting mass transport–concentration overvoltage Eq. (7). Kunimatsu [7] has determined the Tafel's slope of hydrogen evolution in 0.5 M H_2SO_4 on the platinum-coated electrode as 30 mV dec^{-1}. Cardarelli [2] presented hydrogen evolution exchange current density as $i_0 = 0.69$ mA cm^{-2} with the slope of 29 mV dec^{-1} in the solution of 2 M H_2SO_4 and in 1 M HCl $i_0 = 0.63$ mA cm^{-2}, 25 mV dec^{-1}, oxygen evolution reaction exchange current density in 1 M H_2SO_4 (80 °C) was $i_0 = 1.26 \times 10^{-8}$ mA cm^{-2} with the slope of 90 mV dec^{-1}, and for the chlorine evolution in 2 M NaCl was $i_0 = 0.19$ mA cm^{-2} with the slope of 290 mV dec^{-1}.

$$i = i_0 \left\{ \frac{c_{0,ox}}{c_{ox}} \exp\left[\frac{\alpha_C zF}{RT}\eta\right] - \frac{c_{0,red}}{c_{red}} \exp\left[\frac{-(1-\alpha_C)zF}{RT}\eta\right] \right\} \tag{6}$$

$$\eta = \frac{2,303 \cdot RT}{\alpha_C \cdot zF} \log|i_0| + \frac{2,303 \cdot RT}{\alpha_C \cdot zF} \log|i| \tag{7}$$

$$\eta = a + b \cdot \log|i| \tag{8}$$

a, *b*—Tafel equation coefficients, c_0—reactant surface concentration, *c*—bulk concentration, *i*—current density, i_0—exchange current density, α_C, α_A—symmetry coefficient, η—overvoltage, *z*—charge, *F*—Faraday constant, *T*—thermodynamic temperature, *R*—universal gas constant

2. Experimental

Measurement of activation electrode overvoltage was held in modified laboratory ED unit with platinum-coated titanium electrodes (Pt/ATA) with surface area of 64 cm^2. There were recorded polarization curves of the working electrode in three-electrode arrangement using referent saturated calomel electrode (SCE). Measuring was proceeded by current change on the working electrode in the range 0.8–3 A by step 5 mA s^{-1}. It was used as positive polarization for measurement of the anodic reaction of oxygen and chlorine evolution, and negative polarization for the cathodic hydrogen evolution.

Polarization curves were measured in the electrolytes of aqueous solution of salts NH_4NO_3, NaCl, $NaNO_3$, Na_2SO_4, KCl, KNO_3, K_2SO_4 in concentrations 2, 10, 20, and 30 g l^{-1}. The electrolyte was recirculated through module by linear velocity of 3.5 cm s^{-1} with temperature 25 °C.

3. Result and discussion

All polarization curves of the cathodic reaction were of same shape and did not depend on the electrolyte. There was only the hydrogen evolution reaction on the electrode. Just as the hydrogen evolution reaction, the shape of the polarization curves of the oxygen evolution reaction was of the same shape in nitrates and sulfates. Polarization curves of the anodic reaction in the presence of chlorides were different. Fig. 1 had shown a turn in chlorine evolution caused by concentration polarization. In low current densities proceed parallel chlorine and oxygen evolution. At current density of 10 mA cm^{-2} in electrolyte 30 g l^{-1}

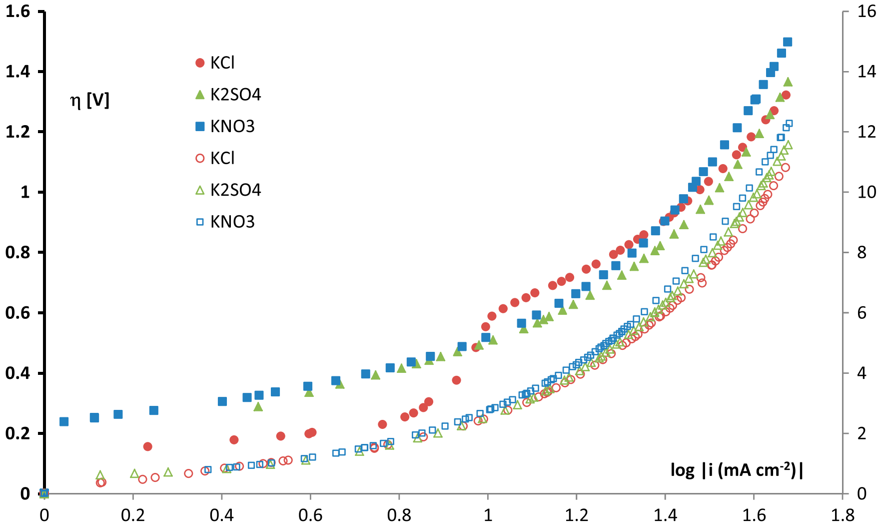

Fig. 1. Anodic polarization curves in electrolytes of variable composition and concentration 2 g l^{-1} (empty symbols) and 30 g l^{-1} (full symbols), η vs. $E = 1.229$ V.

KCl, occurs the overvoltage growth caused by insufficient chloride transport from the electrolyte bulk to the surface of the electrode known as concentration overvoltage. The following increased current density caused only an increase in the reaction rate of the oxygen evolution. Chlorine evolution reaction was proceeded only in the constant limiting rate. In the electrolyte, 2 g l^{-1} of KCl is the turn of concentration overvoltage smaller and moved to the lower current densities at about 0.3 log|*i*|, which implies the position of concentration overvoltage that depends on the chloride concentration and thickness of diffusion layer.

Polarization curves for the cathodic and anodic reaction of hydrogen and oxygen evolution, respectively, in NH_4NO_3 electrolyte in the concentration 2–30 g l^{-1} are shown in Fig. 2. Identical with Doyle [8] work were η vs. log|*i*| curves interspaced by Tafel's

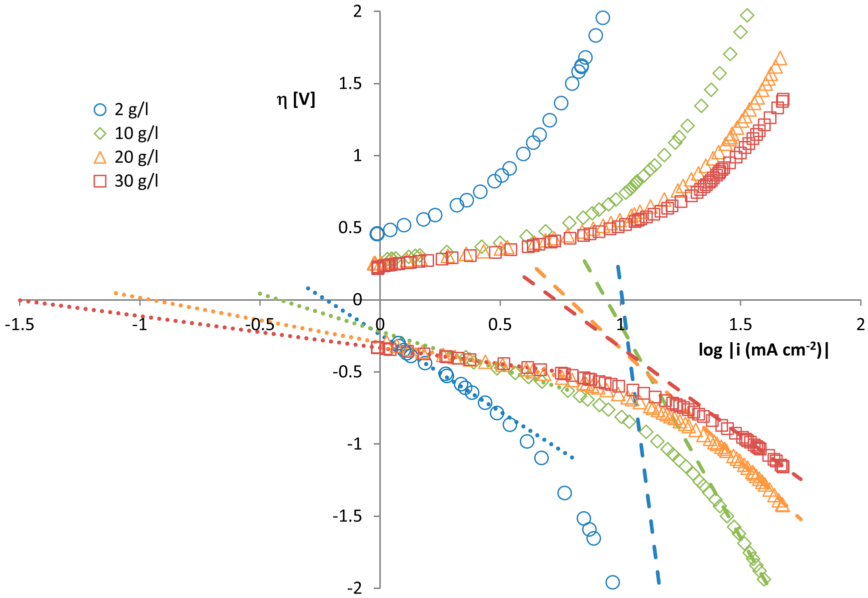

Fig. 2. Tafel's function as slope of cathodic hydrogen evolution reaction in low (dotted) and high (dashed) current densities. Cathodic and anodic polarization curves of NH_4NO_3 electrolyte with variable concentration. Cathodic η vs. $E = 0$ V, anodic η vs. $E = 1.229$ V.

Table 1
Tafel's equation constants, low current densities

	α_C	Cathodic reaction			α_A	Anodic reaction		
c [g l^{-1}]	2	10	20	30	2	10	20	30
Na_2SO_4	0.024	0.048	0.080	0.086	0.026	0.115	0.098	0.154
K_2SO_4	0.017	0.050	0.045	0.094	0.036	0.128	0.100	0.080
NaCl	0.024	0.072	0.081	0.072	0.035	0.085	0.127	0.158
KCl	0.034	0.030	0.048	0.055	0.049	0.205	0.227	0.263
$NaNO_3$	0.017	0.035	0.060	0.114	0.033	0.111	0.127	0.104
KNO_3	0.024	0.063	0.073	0.074	0.020	0.073	0.097	0.131
NH_4NO_3	0.025	0.059	0.083	0.135	0.028	0.127	0.134	0.107
	i_0(C) [mA cm^2]				i_0(A) [mA cm^2]			
Na_2SO_4	0.29	0.13	0.02	0.02	0.30	0.03	0.16	0.06
K_2SO_4	0.95	0.17	0.29	0.02	0.23	0.04	0.13	0.48
NaCl	0.79	0.15	0.21	0.10	0.42	0.36	0.25	0.42
KCl	0.54	2.68	1.62	1.48	0.14	0.07	0.04	0.07
$NaNO_3$	0.73	0.56	0.14	0.01	0.29	0.08	0.07	0.18
KNO_3	0.43	0.10	0.07	0.09	0.67	0.28	0.22	0.10
NH_4NO_3	0.66	0.35	0.17	0.03	0.46	0.07	0.08	0.15

Table 2
Tafel's equation constants, high current densities

	α_C	Cathodic reaction			α_A	Anodic reaction		
c [g l^{-1}]	2	10	20	30	2	10	20	30
Na_2SO_4	0.002	0.006	0.011	0.014	0.001	0.005	0.008	0.011
K_2SO_4	0.002	0.007	0.014	0.017	0.001	0.005	0.008	0.012
NaCl	0.002	0.009	0.016	0.031	0.001	0.006	0.012	0.016
KCl	0.002	0.013	0.020	0.027	0.001	0.006	0.010	0.015
$NaNO_3$	0.002	0.007	0.011	0.024	0.001	0.006	0.010	0.013
KNO_3	0.001	0.007	0.012	0.022	0.001	0.005	0.010	0.013
NH_4NO_3	0.002	0.010	0.015	0.024	0.002	0.007	0.011	0.014
	i_0(C) [mA cm^{-2}]				i_0(A) [mA cm^{-2}]			
Na_2SO_4	13.91	10.44	7.15	6.33	14.15	14.07	13.39	13.00
K_2SO_4	10.87	10.24	6.45	5.62	15.17	14.89	14.05	12.86
NaCl	16.94	11.74	10.11	2.54	15.09	15.43	12.17	10.74
KCl	15.61	7.33	5.63	4.95	15.57	15.86	13.76	10.28
$NaNO_3$	13.70	11.35	8.65	2.57	14.28	11.24	10.63	10.44
KNO_3	14.19	11.06	8.46	3.60	14.17	13.65	11.72	10.25
NH_4NO_3	10.16	9.08	8.94	5.38	12.30	10.99	10.51	10.25

function both for low current densities (1–10 mA cm^{-2}) and for high current densities (25–40 mA cm^{-2}). The symmetric constants α_C or α_A and exchange current densities i_0 were determined from the slope of Tafel's equation Eq. (8) using the expression Eq. (7). Calculated current densities correspond to the intersection of Tafel's plot with $\log|i|$ axis. This method was used for evaluation of the remaining electrolytes. Tables 1 and 2 shows the constants for low current densities and for high current densities, respectively.

4. Conclusion

Dependence of the current density on potential on the real large Pt/ATA electrode was measured for the cathodic and anodic electrode reactions in low concentrated salt electrolytes in range of 2–30 g l^{-1}. Data showed some trends in Butler–Volmer coefficients with increasing of salt concentration and electrolyte specific conductivity. Increasing of salts concentration caused weak drop of the exchange current density of anodic oxygen and chlorine evolution. Decreasing of the exchange current density of cathodic hydrogen evolution reaction was not as significant as for the anodic reaction. The symmetry coefficients were rising with similar slopes for both electrode reactions. Choice of chlorine-free electrolyte has no significant influence on ED power loss on electrode reactions. Using of chloride electrolyte can decrease electrode overvoltage but also cause pollution by free chlorine.

Acknowledgment

The work was supported by the Ministry of Industry and Trade of the Czech Republic within the framework of the project "Research, development and application of new generation electromembrane modules" program TIP No. FR-TI4/398, using the infrastructure of the Membrane Innovation Centre (No. CZ 1.05/2.1.00/03.0084).

References

[1] W. Sheng, H.A. Gasteiger, Y. Shao-Horn, Hydrogen oxidation and evolution reaction kinetics on platinum: acid vs. alkaline electrolytes, J. Electrochem. Soc. 157 (2010) B1529–B1536. doi:10.1149/1.3483106.

[2] F. Cardarelli, Miscellaneous electrical materials, in: Materials Handbook: a concise desktop reference, second ed., Springer, London, 2008, pp. 655–568. ISBN 978-1-84628-669-8. Available from: http://books.google.cz/books?id=PvU-qbQJq7IC&pg=PR4&lpg=PR4&dq=ISBN+978-1-84628-+669-8&source=bl&ots=xDWUognBS3&sig=gwndFJV9OFz8GjEL76Nd7nBDNko&hl=cs&sa=X&ei=2-RhVN2HF MTqaI2hgcgH&ved=0CCMQ6AEwAw#v=onepage&q=IS BN%20978-1-84628-%20669-8&f=false.

[3] A.C.C. Tseung, S. Yeh, X. Liu, G.H. Kelsall, P. Dykstra, Novel acid-resistant oxygen evolution electrodes, commission of the European communities, Stationery Office Books, Brussels, 1991. ISBN: 978-0119727548

[4] P.R. Roberge, Kinetics at equilibrium: The exchange current concept in: Handbook of Corrosion Engineering, McGraw-Hill, New York, 2000. ISBN 0-07-076516-2. Available from: http://www.cntq.gob.ve/cdb/documentos/quimica/197.pdf.

[5] P. Atkins, J. Paula, Elements of Physical Chemistry, W. H. Freeman and Company, New York, 2009. ISBN 978-1-4292-1813-9.

[6] K. Bouzek, Electrochemical engineering (in Czech). ICT in Prague, Prague, 1999. ISBN 80-7080-368-1.

[7] K. Kunimatsu, T. Senzaki, M. Tsushima, M. Osawa, Reaction intermediate of hydrogen evolution reaction on a Pt electrode studied by surface-enhanced infrared spectroscopy, in: 206th Meeting of the Electrochemical society, Honolulu, HI, USA, 2004.

[8] R.L. Doyle, M.E.G. Lyons, An electrochemical impedance study of the oxygen evolution reaction at hydrous iron oxide in base, Phys. Chem. Chem. Phys. 15 (2013) 5224–5237, doi:10.1039/c3cp43464 h.