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Improved deuterium separation factor for the iron electrode prepared in a magnetic field

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Abstract

The electrolytic deuterium separation factors were measured in KOH aqueous solution at 298 K for the two iron films electrodeposited in no magnetic field (film (a)) and a magnetic field of 0.5 T (film (b)). The separation factors were higher for film (b) (9.8–12.3) than those for film (a) (8.7–10.2). From the exchange current density and the real surface area, it was found that film (b) has higher electrocatalytic activity for the hydrogen evolution reaction. The SEM images showed cracks on the whole surface for film (b), which suggests that the strain energy is stored. The improved electrocatalytic activity for the HER is explained by the preferred adsorption of proton due to the strain energy in the film. The increase of the deuterium separation factor is also explained by the electrocatalysis activated by the strain energy. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Deuterium separation; Water electrolysis; Real surface area; Magnetic field; Strain energy

1. Introduction

Heavy water (D_2O) is indispensable as a moderator in fission reactors and together with T (tritium) for the fusion reaction and for the heavy water nuclear reactor. There are several methods to produce heavy water commercially, e.g. hydrogen sulphide–water exchange process [1], ammonia–hydrogen exchange process [1] and water electrolysis process [2]. Among them, water electrolysis has the highest separation factor, therefore, it plays a crucial role in the final separation stage. It is, therefore, very important to develop a cathode material having a high separation factor.

In the practical electrolysis plant, mild steel has been employed as a cathode material for deuterium separation. Its separation factor has been reported to be within the range of 4–7 in 28 wt.% KOH solution [3]. Pure iron is known to be one of the superior materials having high separation factors [4–7]. Brun et al. [6] investigated the electrolytic separation factor at various cathode materials in 10 wt.% KOH and re-

ported that the electrodeposited iron had the highest value around 10.

Bockris et al. [8-10] theoretically investigated the deuterium separation factor using quantum mechanics. The general explanation taken in the literatures is that the deuterium separation factor depends largely upon two factors. One is tunnel effect of the hydrogen isotope. The other is a difference in the zero point energy of the O-H and O-D adsorbed on the metal, which provides an extra effect to the tunnel effect. However, such quantum mechanical approach seems to be possible only for well-clarified electrodes like mercury and single crystals of noble and transition metals. It is very difficult to conduct the quantum mechanical approach on the most of the practical systems, e.g. polycrystalline, various surface microstructure, oxide film and metal alloy. On the other hand, it is well known that the deuterium separation factor is generally high for the electrodes having a high activity for the hydrogen evolution reaction (HER) [11,12]. Therefore, the separation factor is expected to be improved even for the same kind of metals by increasing the electrocatalysis for the HER. In fact, Rowland [13] measured the separation factors for the iron electrodes with different surface conditions in 2.0 M KOH solution and reported that the separation factor for the bare iron was higher than that for the iron covered with an oxide

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film. The cause of this difference was explained by the higher electrocatalytic activity of the bare iron for the HER.

On the other hand, several factors have been reported for increasing the HER electrocatalysis for the same kind of metals. For example, Doyle et al. [14] studied the effect of microstructure of nickel electrode on the HER electrocatalysis in 0.1 M NaOH solution and reported that characteristics of grain boundary and nanocrystalline defects considerably influenced the electrocatalytic activity. Ohmori [15] investigated the HER in 0.1 M NaOH by using nickel electrodes annealed in various temperatures and reported that the electrocatalytic activity depended on the strain energy. This was explained by the occurrence of alkaline metal deposition which adsorbed on the electrode active site instead of hydrogen atom.

On the basis of the above reported results and considerations, the authors considered that a new electrode material having a high separation factor would be obtained by controlling the microstructure and the strain for the electrodeposited iron film. In our previous study, iron films were electrodeposited in uniform magnetic fields (0.5-5 T)and no magnetic field [16], and remarkable difference was found concerning the texture. That is, biaxial texture evolution occurred in magnetic fields (>0.5 T) while uniaxial texture evolution proceeded in no magnetic field. It is easy to estimate that characteristics of the grain boundaries are different from each other for the two iron films. In addition, larger strain should be left for the film electrodeposited in a magnetic field, because iron is a ferromagnetic metal.

In the present paper, the authors actually measured the deuterium separation factor for the iron films electrodeposited in a magnetic field and no magnetic field. The iron films were characterized from the viewpoints of the surface morphology, the texture, the kinetic parameters for the HER and the real surface area. Based on these results, the cause of the difference in the separation factor was discussed considering the grain boundary energy and the strain energy.

2. Experimental

2.1. Preparation of iron electrodes

The electrodeposition apparatus and method have been described in our previous report [16]. Thus, only several important points are mentioned here. The cathode was a sheet of copper ($10 \text{ mm} \times 10 \text{ mm} \times 0.2 \text{ mm}$, Cu 99.99%, Nilaco). The anode was a sheet of iron ($10 \text{ mm} \times 10 \text{ mm} \times 0.2 \text{ mm}$, Fe 99.99%, Nilaco). An electrolyte composition was 0.90 mol l⁻¹ FeSO₄·7H₂O, 0.15 mol l⁻¹ FeCl₂·4H₂O and 0.43 mol l⁻¹ NH₄Cl. The pH was adjusted to 1.5 with H₂SO₄. The solution temperature was maintained at 298 K. The iron electrodeposition was conducted galvanostatically at 10 mA cm⁻² until the amount of electrical charge reached 150 C cm⁻². A uniform magnetic field (0.5 T) by the per-

manent magnet (NEOMAX, Sumitomo Special Metals) was superimposed parallel to the electrode planes.

The texture of the electrodeposited iron film was measured by XRD using Cu K α line (X'Pert, Philips, 50 kV, 40 mA). The morphology was observed by SEM (S-2600H, Hitachi).

2.2. Measurement of polarization curves for the HER and the real surface areas

Fig. 1 shows the electrolytic cell for water electrolysis. The measurement was conducted in $1.0 \text{ mol } 1^{-1}$ KOH aqueous solution at 298 K. The catholyte was separated from the anolyte by a membrane filter. The total volume of the electrolyte was 150 cm^3 . The cathode was the electrodeposited iron film ($10 \text{ mm} \times 5 \text{ mm} \times 0.02 \text{ mm}$). The anode was a sheet of platinum ($20 \text{ mm} \times 20 \text{ mm} \times 0.1 \text{ mm}$, Pt 99.9%, Nilaco). A reference electrode was the reversible hydrogen electrode (RHE).

The real surface area of the iron electrode was determined by ac impedance and initial potential-relaxation methods. The impedance data were acquired by frequency response analyzer (SI 1260, Solartron). The frequency range was from 10 kHz to 0.1 Hz. The impedance spectra were fitted by ZPLOT software (Scribner Associates Inc). The potential-relaxation curves were recorded by digital oscilloscope (NR-2000, Keyence) following the interruption of various cathodic current densities. The measurement time range was 10^{-6} s to 10^{-1} s. The non-linear potential curves were fitted by KaleidaGraph software (Synergy Software).

2.3. Measurement of deuterium separation factors

The same electrolytic cell shown in Fig. 1 was used for the deuterium separation. The electrolyte was $1.0 \text{ mol } 1^{-1}$ KOH with 10 at.% deuterium adjusted by heavy water (D₂O 99.9%, Cambridge Isotope Laboratories). The deuterium separation was conducted galvanostatically at apparent current densities from 50 to 400 mA cm⁻². The evolved



Fig. 1. Schematic electrolytic cell for water electrolysis. A: Sampling bottle; B: cathode (electrodeposited Fe, 1 cm^2); C: Luggin probe; D: anode (Pt, 8 cm^2); E: membrane; F: liquid junction; G: reference; H: Pt black.

hydrogen gas was stored in a sampling bottle. The gathered gas was flowed through the silica gel to remove water impurity from the hydrogen gas. A quadrupole mass spectrometer (AQA-100 MPX, ANELVA) was used to measure the ratio of deuterium to protium.

3. Results and discussion

3.1. Structure of iron electrodes

In the present paper, two types of the iron film electrodes were prepared to study the magnetic field effect on electrode characteristics: film (a), iron film electrodeposited in no magnetic field (0T) and film (b), iron film electrodeposited in a magnetic field (0.5 T).

The surface morphology was observed by SEM, as shown in Fig. 2. In film (a), the surface was uniformly covered with iron grains and no crack was observed. In film (b), the cracks were found on the whole surface while no distinct change was observed in the grain size. Moreover, there is a possibility of the existence of small cracks that cannot be recognized by the present SEM. The occurrence of the cracks suggests the existence of the strain energy induced by a high magnetic field.

In order to investigate surface morphology in detail, AFM observation was conducted. In film (a), the surface of the

(a) $f_{25 \ \mu m}$

Fig. 2. SEM images of the iron films electrodeposited in ferrous sulfate solution at 10 mA cm^{-2} . Film (a) iron electrodeposited in 0 T, film (b) iron electrodeposited in 0.5 T.

iron grains was irregular and angular. In film (b), the surface was roundish and smooth. However, there were no large differences in grain size and surface roughness between the two iron films (Fig. 3).

The metallographic structure was also investigated by the X-ray pole figure measurement. There was a remarkable difference in the film texture. Fig. 4 shows the pole figures of iron (1 1 0) plane. The magnetic field was applied parallel to the substrate surface and its direction was indicated by an arrow in the figure. In film (a), there was an annular symmetric pattern at the angle of 30° to the direction normal to the substrate plane. The angle of 30° indicated that $\langle 2 1 1 \rangle$ plane was preferentially oriented vertical to the film growth direction (electric field direction). The circle pattern indicated that (1 1 0) planes faced arbitrary directions randomly. That is, uniaxial texture evolution along (2 1 1) axis occurred in no magnetic field. On the other hand, in film (b), there was an obvious crystal orientation in same direction of the

(b) 500 nmFig. 3. AFM images of the iron films electrodeposited in ferrous sulfate solution at 10 mA cm⁻².





Fig. 4. Pole figures of iron $\langle 1\,1\,0\rangle$ plane at films (a) and (b) electrodeposited at 10 mA cm⁻². An arrow is a magnetic field direction.

magnetic field at the angle of 30° . It was found that (110) plane was oriented to the magnetic field direction in addition to (211) plane orientation. That is, biaxial texture evolution along (211) and (110) axes occurred in a magnetic field.

3.2. Polarization curves for the HER

The HER at films (a) and (b) was examined in $1.0 \text{ mol } l^{-1}$ KOH solution at 298 K. Prior to the polarization measurement, the films were polarized cathodically at -0.20 V versus RHE for 1 h in order to remove pre-existing oxide film on the electrode surface. Fig. 5 shows steady state polarization curves. The measurement was conducted potentiostatically from -0.05 to -0.50 V, changing the electrode potential by decrements of 0.05 V. Steady state current was obtained after 60s electrolysis at each potential. From these plots, it is clear that both electrodes have one well-defined Tafel region. The kinetic parameters obtained from the Tafel plots are listed in Table 1. The Tafel slopes, b, were almost same for the both films. They were in good agreement with the reported value, 110-160 mV, for iron electrode in alkaline solution [17,18]. On the other hand, the apparent exchange current density, i_0 , was different from each other. The i_0 value of film (b) was about five times higher than that of film (a).



Fig. 5. Steady state polarization curves for the HER at films (a) and (b) in $1.0 \text{ mol } l^{-1}$ KOH solution at 298 K. (\blacksquare) Film (a) and (\bigcirc) film (b).

3.3. Real surface area measurements

The i_0 value is determined by both the intrinsic electrocatalytic activity and the real surface area of the electrode. In order to distinguish these factors, the real surface area was estimated from the interfacial double-layer capacitance by following two methods.

One is the ac impedance method. It was carried out for the HER in $1.0 \text{ mol } 1^{-1}$ KOH solution at four overpotentials: (1) -0.40 V (2) -0.35 V (3) -0.30 V and (4) -0.25 V. Fig. 6 shows complex-plane plots for the HER at films (a) and (b). It can be seen that the center of the semicircles is depressed in both films. The depression is caused by two capacitances interaction, the interfacial double-layer capacitance, C_{dl} , and the hydrogen adsorption pseudocapacitance, C_{ϕ} . [19–21].

The impedance data of the HER can be represented by the equivalent circuit shown in Fig. 7 [22], where R_s is the solution resistance, R_1 the charge transfer resistance, R_2 the adsorption resistance. In the present study, the constant phase element is used for both capacitances in order to compensate for non-homogeneity of the electrode surface.

In Fig. 6, the solid curves represent the best fitting curves while the fitted values of the equivalent circuit elements are listed in Table 2. It was found that the fitting curves are agreed well with experimental plots. According to Table 2, the $C_{\rm dl}$ values were almost constant regardless of the overpotential. The values of films (a) and (b) were 230 ± 5 and $450 \pm 15 \,\mu\text{F cm}^{-2}$, respectively.

The other is potential–relaxation method. The open circuit potential, just after interrupting the cathodic current density,

Table 1 Values of the kinetic parameters for the HER at films (a) and (b)

Type of film	<i>b</i> (mV)	$i_0 (\mathrm{mAcm^{-2}})$	
(a)	143	1.92×10^{-2}	
(b)	138	7.98×10^{-2}	



Fig. 6. Experimental (symbols) and fitted (solid curves) complex plane plots for the HER at four overpotentials (1) -0.40 (2) -0.35 (3) -0.30 and (4) -0.25 V. (Solution: $1.0 \text{ mol } 1^{-1}$ KOH, temperature: 298 K).



Fig. 7. Equivalent circuit used for analysis of the ac impedance data in Fig. 6.

Table 2 Values of the equivalent circuit elements for the data of the ac impedance measurement

Type of film	$-\eta$ (V)	$R_{\rm s}~(\Omega)$	$R_1 (\Omega)$	$C_1 (\mu F)$	$R_2 (\Omega)$	<i>C</i> ₂ (mF)
(a)	0.25	0.605	0.505	225	5.74	5.91
(a)	0.30	0.606	0.509	239	2.17	2.48
(a)	0.35	0.596	0.453	224	1.12	1.97
(a)	0.40	0.623	0.441	227	0.41	1.08
(b)	0.25	0.612	0.173	465	6.66	59.6
(b)	0.30	0.622	0.152	461	2.25	50.8
(b)	0.35	0.628	0.136	476	1.56	45.2
(b)	0.40	0.638	0.123	445	0.73	32.5

is expressed by the following equation [23]

$$-C_{\rm dl}\left(\frac{{\rm d}\eta}{{\rm d}t}\right) = i_0 \exp\left(\frac{\alpha\eta F}{RT}\right) \tag{1}$$

where α is the transfer coefficient and *F* the Faraday constant. Integration of Eq. (1) gives

$$\eta(t) = a - b \log(t + \tau) \tag{2}$$

where $a = -b \log(2.3i_0/bC_{dl})$, $b = 2.3RT/\alpha F$ and the integration constant $\tau = bC_{dl}/2.3i_{t=0}$. Therefore, $\eta(t)$ should be a linear function of $\log t$ for $t \gg \tau$. Also, from the integration constant τ

$$C_{\rm dl} = \frac{2.3i_{t=0}\tau}{b} \tag{3}$$

Consequently, the constants *b* and τ are evaluated by fitting Eq. (2) to the experimental data so that $C_{\rm dl}$ can be calculated from Eq. (3).

The potential was measured at four different cathodic current densities: (1) 6.5 mA cm^{-2} (2) 10 mA cm^{-2} (3) 15 mA cm^{-2} and (4) 20 mA cm^{-2} . The current was maintained for 90 s until the electrode potential reached the steady state value. Then, the open circuit potential transient was recorded after interrupting the current.

Fig. 8 shows the potential-relaxation curves for the HER at films (a) and (b). The circle points and the solid curves



Fig. 8. Experimental (symbols) and fitted (solid curves) potential-relaxation transient curves for the HER at four cathodic current densities: (1) 6.5 (2) 10 (3) 15 and (4) 20 mA cm^{-2} . (Solution: $1.0 \text{ mol} 1^{-1}$ KOH, temperature: 298 K).

stand for experimental data and fitted curves, respectively. Since the experimental data are well fitted by Eq. (2), it is possible to calculate the double-layer capacitance on the iron film. The experimental conditions and the calculated capacitances are listed in Table 3. The values of films (a) and (b) were 200 ± 10 and $350 \pm 10 \,\mu\text{F}\,\text{cm}^{-2}$, respectively. The capacitances were constant regardless of the applied current density for the both films. These values agreed approximately with those obtained by the ac impedance measurement (Table 2).

Since the C_{dl} of film (b) is about twice larger than that of film (a), the real surface area of film (b) can be considered to be about twice larger. This might be explained by cracks that increase the surface area contacting the electrolyte. In this case, small cracks that could not recognized in Fig. 2 would play a major role. On the other hand, the i_0 of film (b) is about five times higher than that of film (a). This cannot be explained sufficiently only by the difference of the real surface area. Therefore, it is suggested that film (b) has the higher electrocatalytic activity for the HER.

3.4. Deuterium separation

The electrolytic deuterium separation was conducted galvanostatically. The deuterium separation factor, α , is defined by the following isotopic abundance ratio [24]

$$\alpha = \frac{([D]/[H])_{l}}{([D]/[H])_{g}}$$
(4)

where [D] and [H] are atomic fractions of deuterium and protium, the subscript (l) refers to the liquid phase and (g) to the gas phase.

In our experiment α is measured after continuous water electrolysis for 8 h since the electrolytic separation requires the duration time to reach a steady state [25]. Fig. 9 shows dependencies of the separation factor on the current density at 298 K. In the figure, circle and square plots stand for films (a) and (b), respectively. The correction for the increase of surface area was made for the current density of film (b). Error bars are standard deviations of three independent experimental data at each current density.

Table 3 The fitted values of i_0 and η in Eq. (2) and the calculated values of $C_{\rm dl}$ for the data of the initial potential-relaxation measurement

Type of film	$i_0 (\mathrm{mA} \mathrm{cm}^{-2})$	$-\eta$ (V)	$C_{\rm dl}~(\mu F)$
(a)	6.5	0.312	195
(a)	10	0.362	197
(a)	15	0.401	209
(a)	20	0.448	192
(b)	6.5	0.313	362
(b)	10	0.344	346
(b)	15	0.377	357
(b)	20	0.410	362



Fig. 9. Dependencies of the deuterium separation factor on the current density in $1.0 \text{ mol } 1^{-1}$ KOH solution including 10 at.% deuterium at 298 K. Error bars are standard deviations. (\blacksquare) Film (a) and (\blacklozenge) film (b).

For film (a), the value of α increased from 8.7 to 10.2 as the current density increased. The values are higher than that of the mild steel used in the commercial plant [3]. This difference might be explained by the impurities in the steel. It was reported that carbon and other metals impurities might act as the catalyst for the unfavorable exchange reaction at the cathode surface as follows [26],

$$HDO + H_2 \rightarrow HD + H_2O \tag{5}$$

In film (b), the effective current density decreased by about one-half from the surface area correction. The values of α were 9.8–12.3, which is higher than those of film (a). The highest value 12.3 was obtained at 210 mA cm⁻². This is the highest separation factor among all kinds of materials at 298 K.

On the basis of above results, it was found that the iron electrode prepared in a magnetic field had high electrocatalytic activity for the HER and is superior in deuterium separation. There are two conceivable factors that could increase the electrocatalytic activity.

Firstly, the effect of grain boundary energy is considered. The grain boundaries have been reported to be active sites for the HER [14,27]. This is explained by that the grain boundaries, whose defects are known as coordinatively unsaturated sites, generally possess higher energy than normal coordination. Therefore, the iron electrode having larger grain boundary energy might be more favorable for the HER. On the other hand, it is reported that the grain boundary energy is larger for larger misorientation angle [28]. Since iron crystal is highly oriented at film (b) where the biaxial texture evolution occurred, the misorientation angle of film (b) is expected to be smaller than that of film (a). In this case, grain boundary energy of film (b) would be smaller than that of film (a), which means that film (b) should be inactive for the HER. Since the experimental results contradict the above inference, it is suggested that the grain boundary energy is not essentially relevant to the increase of the electrocatalytic activity in the present case.

Then, the effect of strain energy is discussed. It was reported that the strain energy of the electrode accelerated the HER in 0.1 M NaOH solution [15]. The mechanism was explained by that the adsorption of proton is preferred to that of alkaline metal ions by the strain energy stored in the electrode surface. As described in Section 3.1, the occurrence of cracks (Fig. 2(b)) suggested that the strain energy is stored in film (b). Therefore, the increase of the separation factor could be explained by the electrocatalysis activated by the strain energy.

4. Conclusion

The two iron films electrodeposited in no magnetic field (film (a)) and a magnetic field of 0.5 T (film (b)) were examined with the aim of developing an electrode material having a high deuterium separation factor.

- The SEM and AFM images of the films showed no large differences in the grain size and the surface roughness except for that film (b) contained cracks on the whole surface, suggesting that the strain energy is stored in the iron film.
- (2) From the X-ray pole figure measurement, the biaxial texture evolution was confirmed for film (b) while the uniaxial texture evolution was found for film (a). The grain boundary energy is considered to be small for film (b) since iron crystal is highly oriented.
- (3) The i_0 values for the HER in $1.0 \text{ mol } 1^{-1}$ KOH solution at 298 K were 1.92×10^{-2} and $7.98 \times 10^{-2} \text{ mA cm}^{-2}$ for film (a) and film (b), respectively. The real surface area was found to be about twice larger for film (b) than film (a) by the C_{dl} measurements. These results conclude that the film (b) has the higher electrocatalytic activity for the HER even after the correction for the real surface area.
- (4) The electrolytic deuterium separation factors measured in 1.0 mol 1⁻¹ KOH at 298 K were higher for film (b) (9.8–12.3) than those for film (a) (8.7–10.2).
- (5) The improved electrocatalytic activity for the HER is explained not by the grain boundary energy, but by the strain energy. The increase of the deuterium separation factor is also explained by the electrocatalysis activated by the strain energy.

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References

- [1] J.L. Aprea, Int. J. Hydrogen Energy 27 (2002) 741.
- [2] D.Lj. Stojic, S.S. Miljanic, T.D. Grozdic, M.M. Jaksic, Bull. Electrochem. 12 (1996) 436.
- [3] M. Benedict, T.H. Pigford, H.W. Levi (Eds.), Nuclear Chemical Engineering, McGraw-Hill, New York, 1981, p. 743.
- [4] M. Hammerli, W.J. Olmstead, B.L. Muju, F.R. Smith, J. Electroanal. Chem. 43 (1973) 45.
- [5] P.R. Rowland, Nature 218 (1968) 945.
- [6] J. Brun, Th. Varberg, W. Gundersen, R. Solli, D.K.N.V.S. Forhandl, 29 (1956) 5.
- [7] B. Topley, H. Eyring, J. Chem. Phys. 2 (1934) 217.
- [8] J.O'M. Bockris, S. Srinivasan, D.B. Matthews, Discuss. Faraday Soc. 39 (1965) 239.
- [9] J.O'M. Bockris, D.B. Matthews, J. Chem. Phys. 44 (1966) 298.
- [10] J.O'M. Bockris, E. Gileadi, R. Haynes, J. Electroanal. Chem. 19 (1968) 446.
- [11] H. Kita, J. Electrochem. Soc. 113 (1966) 1095.
- [12] M. Salmon, B.E. Conway, J. Phys. Chem. 68 (1964) 2009.
- [13] P.R. Rowland, J. Electroanal. Chem. 32 (1971) 109.
- [14] D.M. Doyle, G. Palumbo, K.T. Aust, A.M. Elsherik, U. Erb, Acta Metallurg. Mater. 43 (1995) 3027.
- [15] T. Ohmori, J. Electroanal. Chem. 172 (1984) 123.
- [16] H. Matsushima, T. Nohira, I. Mogi, Y. Ito, Surf. Coat. Technol. 179 (2004) 245.
- [17] L.M. Vracar, D.M. Drazic, J. Electroanal. Chem. 265 (1989) 171.
- [18] H. Alemu, K. Juttner, Electrochim. Acta 33 (1988) 1101.
- [19] D.A. Harrington, B.E. Conway, Electrochim. Acta 32 (1987) 1703.
- [20] L. Bai, D.A. Harrington, B.E. Conway, Electrochim. Acta 32 (1987) 1713.
- [21] R.D. Armstrong, M. Henderson, J. Electroanal. Chem. 39 (1972) 81.
- [22] L. Bai, L. Gao, B.E. Conway, J. Chem. Soc. Faraday Trans. 89 (1993) 235.
- [23] R. Simpraga, G.T. Filho, S.Y. Qian, B.E. Conway, J. Electroanal. Chem. 424 (1997) 141.
- [24] L.I. Krishtalik, V.M. Tsionsky, J. Electroanal. Chem. 31 (1971) 363.
- [25] D.Lj. Stojic, S.S. Miljanic, T.D. Grozdic, N.M. Bibic, M.M. Jaksic, Int. J. Hydrogen Energy 16 (1991) 469.
- [26] J. Brun, W. Gundersen, T. Varberg, D.K.N.V.S. Forhandl, 30 (1957) 29.
- [27] J.Y. Huot, M.L. Trudeau, R. Schulz, J. Electrochem. Soc. 138 (1991) 1316.
- [28] R.L. Colombo, J. Howard, J. Mater. Sci. 4 (1969) 753.