J Appl Electrochem (2007) 37:499–504
DOI 10.1007/s10800-006-9281-1

ORIGINAL PAPER

Sodium molybdate—a possible alternate additive for sodium dichromate in the electrolytic production of sodium chlorate

Ming Li · Zbigniew Twardowski · Felix Mok · Norbert Tam

Received: 3 April 2006 / Accepted: 21 November 2006 / Published online: 13 January 2007

Abstract Sodium dichromate is commonly used in sodium chlorate production to maintain high current efficiency; however, it is also a well documented carcinogen. To reduce the environmental impact, identification of a suitable alternative with similar buffering characteristics to dichromate and without adverse effect on the electrolytic performance of sodium chlorate production is important; sodium molybdate is a good candidate. Molybdate ion and its conjugated acid work as a buffer pair at pH 5–6, a lower and slightly narrower pH window than the typical buffer region of dichromate. Nonetheless, the molybdate buffer works effectively during the electrolytic process by maintaining pH at ~5.9. Although the use of molybdate buffer will lower the overpotential of hydrogen evolution reaction (HER) by ~100 mV, the average off-gas oxygen content is noticeably compromised at 3.6–4.6%, measured using a pilot cell operated at 3 kA $m^{-2}$and 80 °C during a 3-day trial. The resulting current efficiency of 91~ 92% is significantly lower than when dichromate is employed as the process additive (> 96%). Mixtures of different dichromate and molybdate ratio were also investigated in terms of the resulting cathode surface potential.

Keywords Chlorate production · Dichromate · Hydrogen evolution · In situ electro-deposition · Isopolymolybdate · Mo/MoO_2

1 Introduction

In the modern sodium chlorate industry the few remaining opportunities to improve cathode performance are reduction in hydrogen evolution overpotential and elimination of dichromate [1–4]. Sodium dichromate is added to prevent cathodic reduction of hypochlorite and chlorate species by formation of a thin film of chromium hydroxide on the cathodic surface; this is one of the key factors in keeping the current efficiency >96% [1, 5, 6]. Meanwhile, dichromate hydrolyses to form $HCrO_4^-$ in equilibrium with H^+ and CrO_4^{2-}. This buffering system effectively maintains the pH of the solution during electrolysis at about 6, which gives the highest reaction efficiency of chlorate formation [2–4]. However, addition of dichromate brings about several disadvantages; the greatest concern is its carcinogenicity. Although this is minimized in closed-loop plants, there exists a potential for contamination of personnel during chemical preparation, post-treatment and accidental spills. Dichromate in the chlorate liquor must be less than 0.5% during sodium chlorate crystallization, otherwise the crystal product will exhibit a characteristic yellowish colour. To achieve this, the pH of the crystallizer feed liquor must be lowered, to reduce CrO_4^{2-} co-crystallization with sulphate during chlorate crystallization [7]. The overpotential of HER on mild steel is also quite high (~500 mV) in the presence of dichromate, which directly affects the specific power consumption. It is

---

M. Li (✉) · Z. Twardowski (✉) · F. Mok ·
N. Tam
Technology Centre, Aker Kvaerner Chemetics, 8515
Eastlake Drive, Burnaby, British Columbia
Canada, V5A 4T7
e-mail: ming.li@akerkvaerner.com

Z. Twardowski
e-mail: ztwardowski@hyflux-filtech.com

estimated that power consumption can be lowered by 10–15% if the overpotential of HER is reduced by 100 mV [1].

Many publications and patents have described the electroplating of Mo alloys onto different substrates at pH 7–9 from a typical molybdate bath, yielding desired electrocatalytic properties for HER [8–10]. Even at a lower pH of 3.5, deposition of Mo was also reported using a pulse-plating method [11]. According to the potential-pH equilibrium diagram, Mo can be electrodeposited over a very wide pH region from –2 to 13, when the potential is lower than –0.4 V vs. standard hydrogen electrode (SHE) [12]. On the other hand, molybdenum oxides, especially MoO_2, were also reported to be formed at a pH of 2–5.5 from certain molybdate baths [13, 14]. To date, in situ electrodeposition of Mo/MoO_2 in a chlorate cell has not been reported. We do not expect in situ electroplating in the chlorate solution to give equivalent Mo films to those obtained in specially optimised baths. However, as long as some electrodeposition of Mo occurs, the electrocatalytic action should lower the surface overpotential on a continuous basis. Hence, continuous electrodeposition of Mo, effected by replacement of the toxic dichromate additive with molybdate, would appear to be a promising strategy to eliminate Cr (VI) species from the chlorate process, as well as lowering the overall cell voltage.

In acidic solution, molybdate anions may condense to form iso-polymolybdate anions with a polymeric structure [12, 15]. At pH 2–3 polysilicamolybdate anions can also be formed with addition of sodium metasilicate to a molybdate solution [15]. These isopolyanions could have a positive influence on cathodic or anodic reactions, thus lowering HER overpotential and/or off-gas O_2 level in our application. In this paper we also report for the first time the effect of polysilicamolybdate anions on the chlorate electrolysis process.

2 Experimental

An in-house setup was used to measure the cathode surface potential vs. the saturated calomel electrode (SCE), as seen in Fig. 1. In this way, the cathode surface potential can be monitored during electrolysis.

A galvanostat and power booster (EG&G Princeton Applied Research) were employed to apply constant current to the cell. A portable pH meter (Accumet, Fisher) was used to measure pH. All reported surface potentials were referenced to SCE (Accumet, Fisher), if not otherwise specified. Photos were taken using a digital Camera (Olympus C-740 Ultra Zoom).

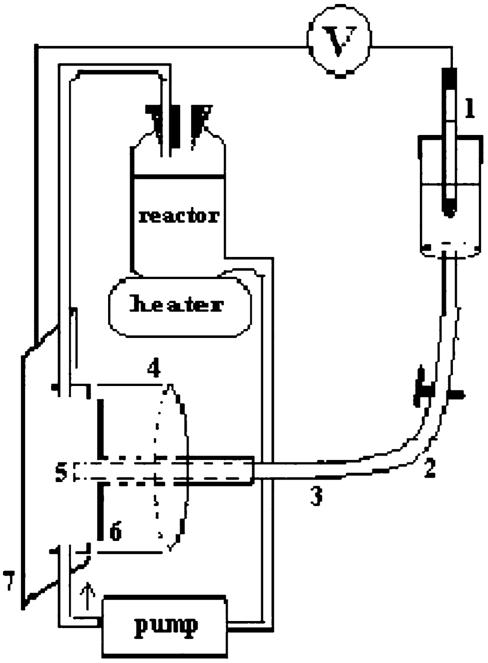

Fig. 1 Schematic of the small lab cell for electrolysis and cathode surface potential measurement. 1: SCE; 2: Soft tubing; 3: Adjustable tubing; 4: Cylindrical electrolyzing cell; 5: Capillary hole; 6: Disc DSA anode; 7: Mild steel plate cathode

The initial concentration of electrolyte in the small cell (see Fig. 1) was 410 g l^{-1} $NaClO_3$ (Nexen Chemicals, 99.5%), 140 g l^{-1} NaCl (Fisher, 99.9%) and 8 g l^{-1} Na_2MoO_4(Anachemia, 99.5%). The electrodeposition was carried out at 2 kA m^{-2} and 80 °C in the small cell. The counter electrode was a typical DSA®(Dimensionally Stable Anode), cut from a commercial size chlorate anode used for modern chlor-alkali and chlorate industries. A pilot cell (similar to Fig. 1 but much larger) was used for the long-term testing starting with 300 g l^{-1}brine solution and 8 g l^{-1}Na_2MoO_4. With that cell, the off-gas O_2 could be reliably measured using a portable O_2 analyzer (Teledyne Analytical Instruments). The pilot cell operated at a current density of 3 kA m^{-2} and the temperature was 80 °C. Standard silica solution (1000 mg l^{-1} as SiO_2, HACH) was used to form polysilicamolybdate anions.

3 Results and discussion

3.1 Comparison of buffer capacity between molybdate and dichromate

As mentioned before, one of the advantages of dichromate is its appropriate buffer range. Chlorate formation includes three reactions [3]:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (1)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (2)$$

$$2HOCl + OCl^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \quad (3)$$

Cl_2 in Reaction (1) is produced from the anodic reaction, $2Cl^- \rightarrow Cl_2 + 2e^-$. Maintaining pH at ~6 provides the optimum reaction rate for the formation of chlorate [Reaction (3)]. At the cathode, the principal reaction is the reduction of water to hydrogen and hydroxide ions:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (4)$$

Since pH has a tendency to increase with the formation of OH^- in Reaction (4), a buffering environment is very important to maintain high reaction efficiency. When $Cr_2O_7^{2-}$ dissolves in water, $HCrO_4^-$ is formed together with a conjugated part of CrO_4^{2-}, with a characteristic pKa of 6.45. Mo belongs to the same group as Cr, and the $HMoO_4^-$—MoO_4^{2-} system has a pKa of 6.0. Figure 2 demonstrates buffer regions of molybdate and dichromate at the room temperature of 22–23 °C, without electrolysis occurring. Buffer regions are observed to be pH 5.0–6.0 for molybdate and 5.0–6.5 for dichromate. Dichromate has a better buffer "fit" considering pH 6.0 to be the optimum for the chlorate reaction [3]. However, this is only a rough comparison as these species could exhibit different buffering properties at a higher temperature and during electrolysis. Buffering by molybdate has been observed to be very effective in the pilot cell. Figure 3 shows the trend of pH with electrolysis time at 3 kA m^{-2} without feeding acidified brine solution. Normally acidified brine solution is added every 30 min to the pilot cells to maintain the effective chloride content. Therefore, as far as maintaining optimum process pH is concerned, molybdate is a suitable substitute for dichromate.

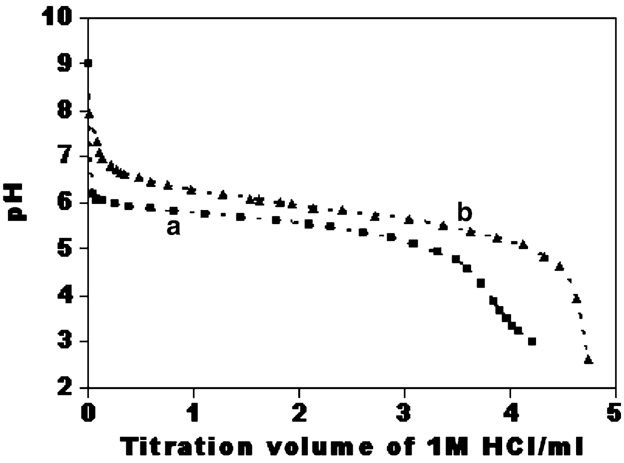

Fig. 2 Buffer region test in the 100 ml chlorate solution for (**a**) molybdate and (**b**) dichromate at room temperature of 23 °C

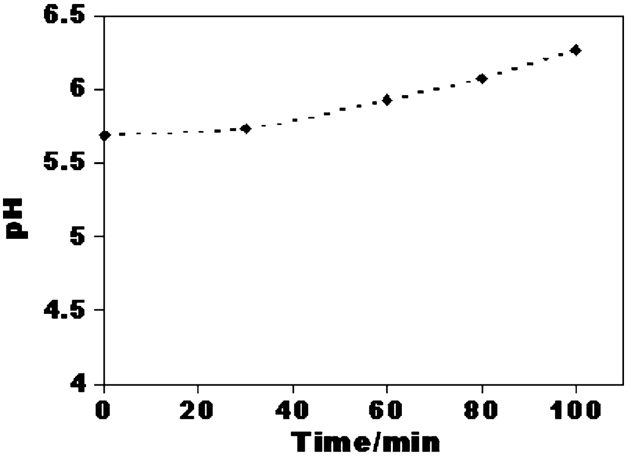

Fig. 3 pH changing with electrolysis time at 3 kA m^{-2}in the pilot cell without feeding acidified brine solution with molybdate additive

3.2 Cathode surface potential (CSP) and current efficiency in the small cell

Figure 4a illustrates the appearance of a mild steel cathode surface after electrolysis with molybdate, which is very different from the mild steel surface without electrolysis (Fig. 4b) and also different from that after electrolysis with dichromate (Fig. 4c). The dark brown-purple deposit in Fig. 4a could possibly be a mixed coating of MoO_2 and Mo formed during in situ electroplating. With the formation of Mo, it is not surprising to obtain a CSP of 1.28 V, which is 110 mV lower than the CSP (1.39 V) obtained with dichromate additive. We are comparing the absolute value of CSP when we talk about "lower" or "drop". Lower CSP means lower HER overpotential and thus better cathode performance. Lowering the hydrogen evolution overpotential is a primary objective for improving the power efficiency of the sodium chlorate process and has been pursued for years [1, 16, 17]. A key advantage brought about by using molybdate is the reduction of HER overpotential. Previous studies have shown that Mo, when in combination with other metals such as Fe, Co, Ni, catalyses the HER [18]. Elezović et al.'s studies demonstrated that an increase in activity could be attributed to an increase in the real active surface area, which, in turn, was directly proportional to the molybdenum content [18]. On the other hand, according to Pourbaix [12], Mo has a slight tendency to

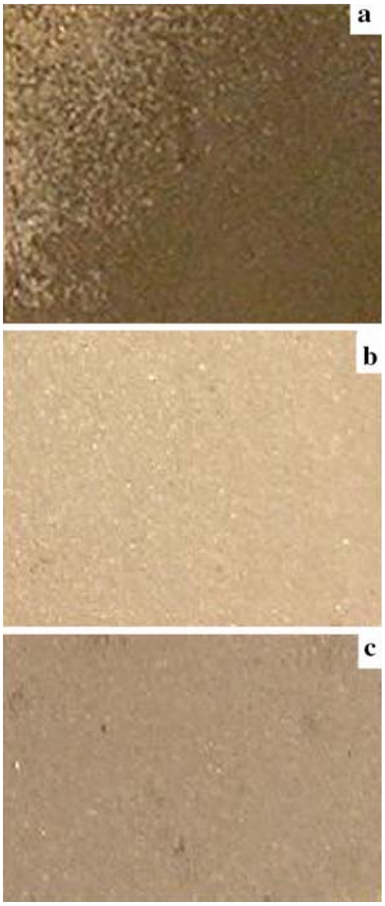

Fig. 4 Digital photos of the mild steel surface (**a**) after electrolyses with molybdate; (**b**) before any electrolyses; (**c**) after electrolyses with dichromate

decompose water (with hydrogen evolution) when present in alkaline solutions. This fact might explain Mo's catalytic behaviour in HER, considering that the solution pH in the thin layer next to the cathode surface is higher than in the bulk.

It is necessary to confirm that hydrated MoO_2 can form an effective barrier that prevents the electroreduction of ClO^- and ClO_3^- species. The current belief in the chlorate industry is that formation of a thin $Cr(OH)_3$ layer is what keeps ClO^- and ClO_3^- from being reduced, thus maintaining a high current efficiency [1]. A substitute for dichromate must exhibit similar characteristics. Fortunately, a barrier of MoO_2 was formed on the mild steel cathode surface preventing ClO^- and ClO_3^-species from being reduced. HER was catalysed at the same time due to the presence of metallic Mo. The co-deposition of Mo/MoO_2 confirms our observation of a lower CSP and acceptable current efficiency (see discussions in next paragraph), but further analyses by XRD or XPS should be conducted to support this assumption.

Figure 5 shows the correlation between current efficiency and solution pH. Current efficiencies were calculated indirectly by measuring collected cell off-gas (H_2). The current efficiency ranges from 85% to 92% at pH lower than 5.7 and increases to ~98% in the pH range 5.75 to 5.95 and drops again above pH 5.95. It must be emphasized that the cell off-gas is mainly composed of H_2 and the calculated current efficiency above is only an approximation. In reality, it will always contain some O_2 and Cl_2. Nevertheless, the overall trend of observed current efficiencies vs. pH is qualitatively valid. At lower pH of ~5.4, Mo oxides are likely to form at the cathode and adversely affect the current efficiency [13, 14]. At higher pH of 7–10, Mo electrodeposition becomes a main cathodic parasitic reaction with the effect of significantly lowering the current efficiency [8–10] (see Fig. 5).

3.3 Off-gas oxygen level in the pilot cell during a long-term testing

Off-gas O_2 level is an important indicating parameter for both chlorate cell current efficiency and safe cell operation, due to the explosive limits of H_2 in O_2 (lower limit at 4.65% and upper limit at 93.9%). Figure 6 shows the percentage O_2 in cell off-gas vs. time during a 60-hour electrolytic pilot cell operation with sodium molybdate additive. The measured off-gas O_2 level was observed to fluctuate between 3.7% and 4.8%. At these values, the O_2 levels are unacceptable for both criteria, as the current efficiency is only about 91% after 55 hours of operation and the H_2 explosive upper limit was nearly reached (with 4.8% O_2). The high off-gas O_2 levels clearly show the adverse influence of molybdate on the DSA® anode, because O_2 is only generated from the anodic parasitic reactions [3].

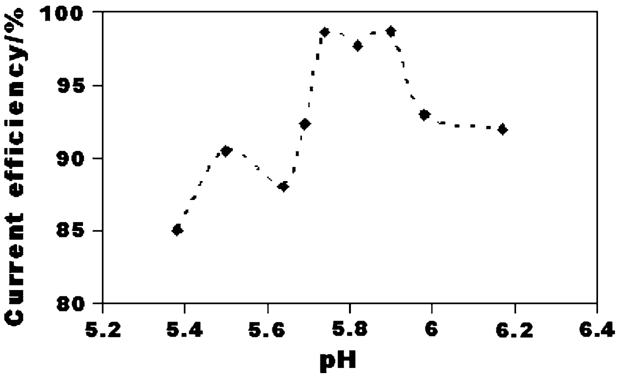

Fig. 5 Current efficiency indirectly measured by collecting cell off-gas (H_2) product as a function of pH during electrolysis with molybdate additive

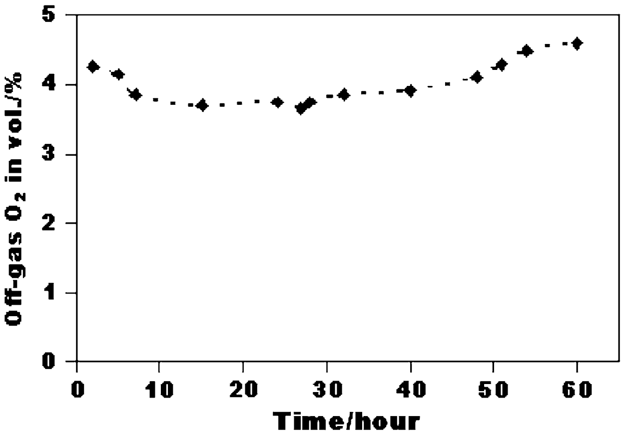

Fig. 6 Off-gas O_2 level in the produced gas (mainly H_2) with a long time scale during the electrolysis with molybdate

A recent study by El-Moneim et al. on nano-crystalline, electrodeposited Mn–Mo–W oxide catalytic anodes reported current efficiencies of 99.8% for oxygen evolution in the electrolysis of acidic seawater [19]. These anodes were prepared by anodic deposition on IrO_2/Ti using $MnSO_4$, Na_2MoO_4 and Na_2WO_4 electrolytes at pH 1.0 [19]. This finding substantially supports our conclusion that the high O_2 level observed in the cell off-gas of our pilot cell could be due to the electrodeposition of Mo oxide onto the DSA® anode. However, no visible colour changes (indicative of this possible weak side reaction) were observed on the anode surface.

In an effort to minimize and control this adverse anodic effect of molybdate on the anode, silica solution was added to the chlorate cell to form polysilicamolybdate anions. The silica concentration was increased in both the small cell and pilot cell from a normal level of 10 mg l^{-1} to a concentration of 50 mg l^{-1} (as SiO_2) and the pH was adjusted to 5.5–6.0. Although this pH range is not optimal for polysilicamolybdate anion formation (which is usually in the 2 to 3 pH region) [12, 15], a characteristic, but faint, yellow colour was still evident. No noticeable change was observed on the CSP and cell voltage, but the O_2 level in the cell off-gas dropped from 4.8% to 4.3%. Although this is not a significant change, it shows that a possible way of lowering the off-gas O_2 level is by formation of molybdate isopolyanions. Disintegration of the isopolyanions during electrolysis in the high pH solution layer next to the cathode surface could explain why no noticeable effects were observed on CSP.

3.4 Performance of mixed molybdate and dichromate in the reduction of CSP

Since pure molybdate shows a very low CSP but poor current efficiency and pure dichromate produces the opposite effect, the combination of the two additives may provide a solution to acceptable cell performance. Table 1 shows CSP at different mass ratios of the additive mixtures during electrolyses.

The CSP with pure molybdate is ~–1.29 V, which is lower than that (~–1.40 V) with pure dichromate by ~110 mV. The surface potential of mixed additives lies in between the potentials of pure molybdate and pure dichromate, as shown in Table 1. The lowering of the CSP is proportional to the increase in molybdate concentration when dichromate is at 2.5 g l^{-1}. However, when dichromate is 4 g l^{-1} and molybdate concentration was varied from 1 to 10 g l^{-1}, the CSP only dropped by 10–20 mV and the decrease was not linear with increase in molybdate. Previously, 3.5 g l^{-1} of dichromate was determined to be the critical concentration for acceptable cell performance in chlorate electrolysis. However, these results show that there is competition between dichromate and molybdate for cathodic influence. Above 3.5 g l^{-1} of dichromate, molybdate was totally excluded in determining the cathode surface potential at pH 6. Figure 7 shows CSP as a function of pH with a mixture of dichromate (4 g l^{-1}) and molybdate (4 g l^{-1}) at 2 kA m^{-2} and 80 °C. It was clearly observed that CSP dropped with decreasing pH, reaching its minimum of 1.33 V at pH ~6.7 before trending up again.

The extent of the many competing reactions occurring at the cathode is still not well understood. Although CSP is lowered substantially at pH 6.7, this pH is outside the buffer region and is not optimum for the chlorate reaction. On the other hand, increased complexity resulting from adding one more compound would counteract the advantage of the reduction of HER overpotential. Nevertheless, this approach of electroplating catalytic coating in situ opens a good opportunity for reducing the HER overpotential in industrial electrolyses.

Table 1 Cathode surface potential (vs. SCE) at different mass ratios of molybdate and dichromate at pH ~6.0, 2 kA m^{-2} and 80 °C

Concentration of additives	Na_2MoO_4: 8 g l^{-1}	Na_2MoO_4: 5 g l^{-1} $Na_2Cr_2O_7$: 2.5 g l^{-1}	Na_2MoO_4: 3.8 g l^{-1} $Na_2Cr_2O_7$:2.5 g l^{-1}	Na_2MoO_4: 1~ 10 g l^{-1} $Na_2Cr_2O_7$:4 g l^{-1}	$Na_2Cr_2O_7$:5 g l^{-1}
CSP/V	–1.28 to –1.30	–1.32	–1.35	–1.38 to –1.39	–1.40 to –1.41

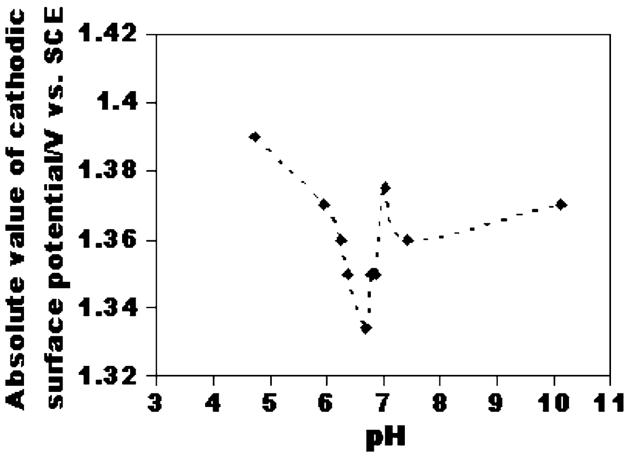

Fig. 7 Cathode surface potential (vs. SCE) as a function of pH with 4 g l^{-1} molybdate and 4 g l^{-1} dichromate

4 Conclusion and future work

In this work molybdate was used to replace dichromate in the sodium chlorate process. This substitution shows a comparable buffer capacity, an environmental compatibility, and a reduction of hydrogen evolution overpotential by 100–130 mV. Replacement of toxic dichromate with molybdate will result in a similar and effective buffer system. However, molybdate interferes with the anodic reaction and incurs a high, unfavourable off-gas O_2 level. Hence, the feasibility of this approach is questionable. Further investigation employing XRD and/or XPS could confirm the formation of MoO_x at the anode.

Acknowledgements The authors thank the Natural Science and Engineering Research Council of Canada (NSERC) for its Industrial R&D Fellowship fund. English edition and revise by our colleague, Ms. Anca Brincus are deeply appreciated.

References

1. Cornell A, Simonsson D (1993) In: Jeffery TC, Fenton J, Ota K, Kawamoto H (eds) Procedings of the symposium on Chloro-Alkali and Chlorate Production and New Mathematical and Computational Methods in Electrochemical Engineering, PV 94–20. The Electrochemical Society, Pennington, pp 191–200
2. Hardee KL, Mitchell LK (1989) J Electrochem Soc 136:3314
3. Viswanathan K, Tilak BV (1984) J Electrochem Soc 131:1551
4. Janssen LJJ, Van der Heyden PDL (1995) J Appl Electrochem 25:126
5. Lindbergh G, Simonsson D (1990) J Electrochem Soc 137:3094
6. Cornell A, Lindbergh G, Simonsson D (1992) Electrochim Acta 37:1873
7. Buckley HE (1931) Z Krist 81:157
8. Murase K, Ando H, Matsubara E, Hirato T, Awakura Y (2000) J Electrochem Soc 147:2210
9. Ananth MV, Parthasaradhy NV (1989) J Electrochem Soc India 38:229
10. Chassaing E, Cornet M, Kinh VQ (1978) Surf Technol 7:145
11. Rengakuji S, Takuno T, Nakamura Y, Ikeno S, Shimasaki C (1998) Denki Kagaku Oyobi Kogyo Butsuri Kagaku 66:754
12. Deltombe E, De Zoubov N, Pourbaix M (1974) In: Pourbaix M (ed) Atlas of electrochemical equilibria in aqueous solutions. National Association of Corrosion Engineers, Cebelcor, pp 272–279
13. Gomez E, Pellicer E, Valles E (2005) J Electroanal Chem 580:238
14. Korobov VI, Loshkarev YM, Kozhura V (1998) Russ J Electrochem (Translation of Elektrokhimiya) 34:1154
15. Jeannin Y, Fournier M (1983) In: Pope MT (ed) Heteropoly and isopoly oxometalates. Springer-Verlag, Berlin, p 43
16. Jin S, Van Neste A, Ghali E, Guay D, Schulz R (1997) Mater Sci Forum 923:235–238
17. Razafitrimo H, Blouin M, Roue L, Guay D, Huot J, Schulz R (1999) Mater Sci Forum 513:312–314
18. Elezović NR, Jović VD, Krstajić NV (2005) Electrochim Acta 50:5594
19. El-Moneim AA, Kumagai N, Asami K, Hashimoto K (2005) Mater Trans 46:309