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Electrochemical behaviour of manganese and molybdenum mixed-oxide anodes in chloride- and sulfate-containing solutions

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The interaction between adsorbed chloride ions and the surface of $Mn_{1-x}Mo_xO_{2+x}\cdot nH_2O$ anodes at pH < 6.0 (in the vicinity of the anode during the electrolysis of neutral chloride solutions) leads to electrode material degradation.

Mixed-oxide $Mn_{1-x}Mo_xO_{2+x}\cdot nH_2O$ anodes have been used for the electrodialysis of seawater to prevent chlorine evolution at the anode.[1–3] The selective evolution of oxygen was observed at these electrodes[1–3] during the anode polarization in chloride-containing solutions, whereas chlorine evolution was almost completely inhibited. However, the use of $Mn_{1-x}Mo_xO_{2+x}\cdot nH_2O$ is limited to alkaline solutions with pH ⩾ 8.0. The degradation of a $Mn_{1-x}Mo_xO_{2+x}\cdot nH_2O$ active layer occurs even under these conditions.[2] No information concerning the origin of selectivity of the $Mn_{1-x}Mo_xO_{2+x}\cdot nH_2O$ anodes in chloride-containing solutions was reported previously.[1–3]

$Mn_{1-x}Mo_xO_{2+x}\cdot nH_2O$ can also be applied to the electrolysis of SO_4^{2-} and SO_4^{2-} + Cl^- containing solutions for electrosynthesis.[4] Note that the electrochemical evolution of oxygen results in significant acidification of the solution at the anode surface. The aim of this work was to estimate the selectivity and durability of $Mn_{1-x}Mo_xO_{2+x}\cdot nH_2O$ anodes in chloride and sulfate solutions.

The $Mn_{1-x}Mo_xO_{2+x}\cdot nH_2O$ anodes were prepared electrochemically as described elsewhere.[1] The oxide materials were deposited on the Ti/IrO_2 electrode surface. The MnO_2 anodes were prepared under the same conditions.[†]

Polarization measurements were carried out in a three-electrode cell. The cathode and anode compartments were separated by a ceramic Al_2O_3 diaphragm. A platinized titanium mesh was used as a cathode. The electrode potentials were measured against an AgCl/Ag electrode (in chloride-containing solutions) and Hg_2SO_4/Hg electrode (in solutions containing no Cl^- ions) and converted to a standard hydrogen electrode (s.h.e.). The ohmic potential drop between the Luggin–Gaber capillary and the working electrode was calculated from *E*–*t* relationships after polarization switching. The polarization measurements were performed in the presence of buffer solutions based on NaH_2PO_4–Na_2HPO_4 and H_3PO_4–NaH_2PO_4 mixtures.

The chlorine concentration in anode gases was determined by iodometric titration; both the gas mixture and the anolyte were analyzed. A Pt/Pt electrode was used to determine the redox potential of synthesized anolytes.

The mixed oxide material including 15–20 at% Mo was formed at the anode in the course of electrolysis (i = 0.01–0.10 A cm^{-2}, 90 °C) in a solution containing Mn^{II} and Mo^{VI} compounds. Stepwise deposition with gradually increasing current density (0.01, 0.03, 0.06 A cm^{-2}) prevented the formation of through-thickness cracks and made the distribution of elements over the sample surface uniform. The durability of anodes prepared in this manner was improved significantly.[4]

The obtained deposits were X-ray amorphous: γ-MnO_2[1] reflections detected for deposits with a zero content of molybdenum almost disappeared when the concentration of Mo in the deposits exceeded 15 at%. The molybdenum oxides act as amorphization agents. The BET specific surface area of $Mn_{1-x}Mo_xO_{2+x}\cdot nH_2O$ was significantly higher than that of $MnO_2\cdot nH_2O$ prepared under the same conditions (120.3 and 270.5 m^2 g^{-1}, respectively). On the other hand, the introduction of molybdenum oxides into the anode deposits had hardly any effect on the isoelectric point in solutions of sodium sulfate (~5.6 at $c_{Na_2SO_4}$ = 0.01–0.50 mol dm^{-3}, which is in good agreement with published data[5]).

The presence of molybdenum oxides in the anode material leads to a significant rise in its durability at anodic potentials in non-buffered Na_2SO_4 solutions. For $Ti/IrO_2/MnO_2$ electrodes, anodic currents over a potential range of 1.15–1.30 V were detected. These currents reached 4×10^{-3} A cm^{-2} and corresponded to the reaction $MnO_2 + 2H_2O \rightarrow MnO_4^- + 4H^+ + 3e$.[2,4,6] The formation of permanganate ions was confirmed by the colour of solution during anode polarization (1.25 V); the spectra of the anolyte indicated the presence of MnO_4^- ions. For $Ti/IrO_2/Mn_{1-x}Mo_xO_{2+x}$ electrodes, currents over the given potential range were much lower and did not exceed 5×10^{-4} A cm^{-2}. Apparently, the formation of an amorphous structure in the course of anodic deposition increased the durability of the oxide material.

In contrast, in non-buffered 0.5 M NaCl solution, the colouration due to MnO_2 colloid formation occurred during electrolysis. Hence, $Mn_{1-x}Mo_xO_{2+x}\cdot nH_2O$ anodes are unstable in chloride-containing solutions without buffer additives.

Anolytes prepared by electrolysis (in Na_2SO_4 solutions) with the use of $Ti/IrO_2/Mn_{1-x}Mo_xO_{2+x}$ anodes were characterized by a lower redox potential ($E_{red\text{-}ox}$ = 0.58 V) than that of anolytes obtained at Pt anodes (0.65 V) at pH 2.8. This fact agrees with the previous results[4] for $Mn_{1-x}Mo_xO_{2+x}$ and IrO_2 anodes. Lower redox potentials of the anolyte prepared with the use of $Mn_{1-x}Mo_xO_{2+x}$ anodes can be caused by a lower concentration of active oxygen species,[7] such as H_2O_2, $HO_2^{\bullet}$, HO_2^- and singlet oxygen. Oxygen in gases evolved at the anode at E > 1.4 V is formed from the oxide layer at the anode surface.[8,9] The metal–oxygen bond enthalpies for Pt, Ir, Mn and Mo oxides are different and this leads to dissimilar content of various oxygen forms in the anolyte prepared by electrolysis.

In the course of electrolysis in Cl^--containing buffer solutions (c_{Cl^-} ⩽ 0.6 mol dm^{-3}), no chlorine evolution was observed at pH 8.0–3.0. In spite of this fact, the cause of the anode material selectivity towards oxygen evolution can be different at various

† Deionized water purified in a Milli-Q system (Aldrich) and extra pure grade reagents were used.

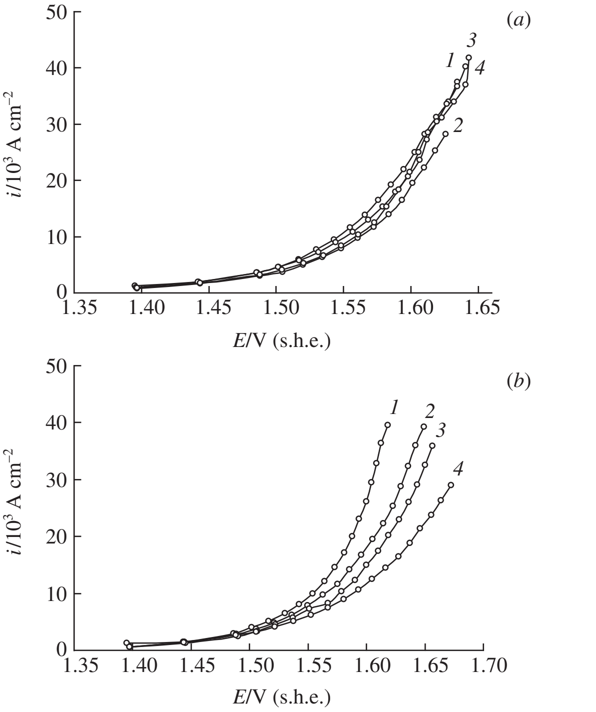

Figure 1 Stationary polarization curves at $Mn_{1-x}Mo_xO_{2+x}$ electrodes in the presence of buffer systems at constant ionic strength. pH (*a*) 8.0 and (*b*) 4.0. Concentration of Cl^- ions (mol dm^{-3}): (*1*) 0, (*2*) 0.05, (*3*) 0.10 and (*4*) 0.5.

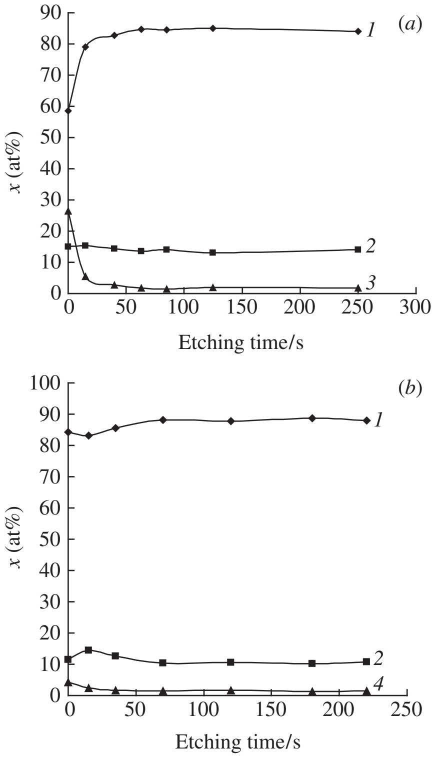

Figure 2 Element concentrations in the surface layers of $Mn_{1-x}Mo_xO_{2+x}$ after long-time electrolysis in (*a*) 0.5 M NaCl and (*b*) 0.5 M Na_2SO_4 solutions *vs.* etching time (by Ar^+ ions). The electrolysis conditions: 10 h, 0.10 A cm^{-2}. (*1*) Mn, (*2*) Mo, (*3*) Cl and (*4*) S.

pH. At pH > 6.0, the replacement of chloride by sulfate (in buffer solutions) exerts no effect on polarization curves [Figure 1(*a*)]. On the other hand, in acid buffer solutions (pH < 6.0), the introduction of Cl^- ions shifts the polarization curves to more positive potentials [Figure 1(*b*)]. Since chlorine does not evolve at the anode, the polarization curves correspond to oxygen evolution. At pH > 6.5, the surface of $Mn_{1-x}Mo_xO_{2+x}$ has a negative charge, and Cl^- ions are not adsorbed at the anode. For this reason, they do not affect the kinetics of O_2 evolution. At pH < 6.0, chloride ions are adsorbed at the active centers of the anode surface to inhibit oxygen evolution. Thus, one can assume interaction between Cl^- ions and oxide material at pH < 6.0. The next step of chlorine evolution (*e.g.*, the discharge of adsorbed chloride ions[10]) is strongly inhibited, and Cl_2 does not evolve at the anode. Note that pH 6.0 is close to an isoelectric point of $Mn_{1-x}Mo_xO_{2+x}$, which was evaluated from potentiometric titration.

The adsorption of chloride ions at the $Mn_{1-x}Mo_xO_{2+x}$-anode surface in the course of electrolysis in non-buffered solutions was confirmed by X-ray photoelectron spectroscopy (XPS)[‡] [Figure 2(*a*)]. After the long-time electrolysis of non-buffered NaCl solutions (0.5 mol dm^{-3}, 10 h, 0.10 A cm^{-2}), a significant amount of chlorine was detected in the electrode surface layers. (Taking into account the fact that a great quantity of carbon is usually detected at the surface of electrode deposits,[11] we normalized XPS data to the sum of manganese, molybdenum and chlorine contents as 100%). High-resolution spectra [Figure 3(*a*)] suggest that all the detected Cl is in the form of chloride ions, which means that no ion discharge to Cl^0 (or Cl^+) occurs during the electrolysis. On the other hand, no significant accumulation of sulfur (from sulfate ions) was observed in the electrode surface layers as a result of long-term electrolysis in Na_2SO_4 solutions [Figure 2(*b*)]. The establishment of a low pH value for the anode region during the electrolysis of a 0.5 M NaCl solution was confirmed by high-resolution spectra for O 1*s* XPS [Figure 3(*b*)], which show a peak at 534 eV corresponding to the protonated form of OH groups at the oxide material surface ($M–OH_2^+$).

On the other hand, no adsorption of Cl^- ions at the $Mn_{1-x}Mo_xO_{2+x}$ electrode surface was detected by XPS at pH 8.0 in a sodium chloride solution (in the presence of a buffer system, Figure 4). The XPS data confirm the adsorption of Cl^- ions in weakly acidic media (or in non-buffered solutions, Figure 2) and no adsorption in a weakly alkaline solution (pH 8.0, Figure 4). It should be taken into account that experiments at pH 8.0

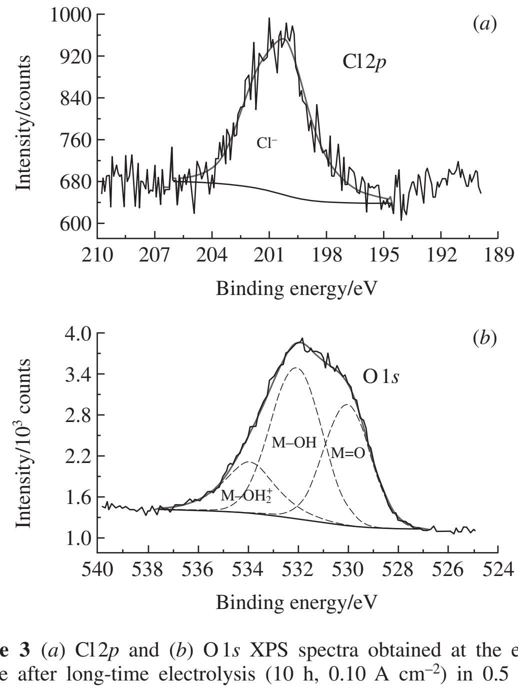

Figure 3 (*a*) Cl 2*p* and (*b*) O 1*s* XPS spectra obtained at the electrode surface after long-time electrolysis (10 h, 0.10 A cm^{-2}) in 0.5 M NaCl solution.

‡ The XPS studies were performed using a PHI 5500 ESCA X-ray photoelectron spectrometer (Physical Electronics) with monochromatic AlKα radiation ($h\nu$ = 1486.6 eV). The phase composition of oxide materials was determined by X-ray phase analysis (CuKα radiation).

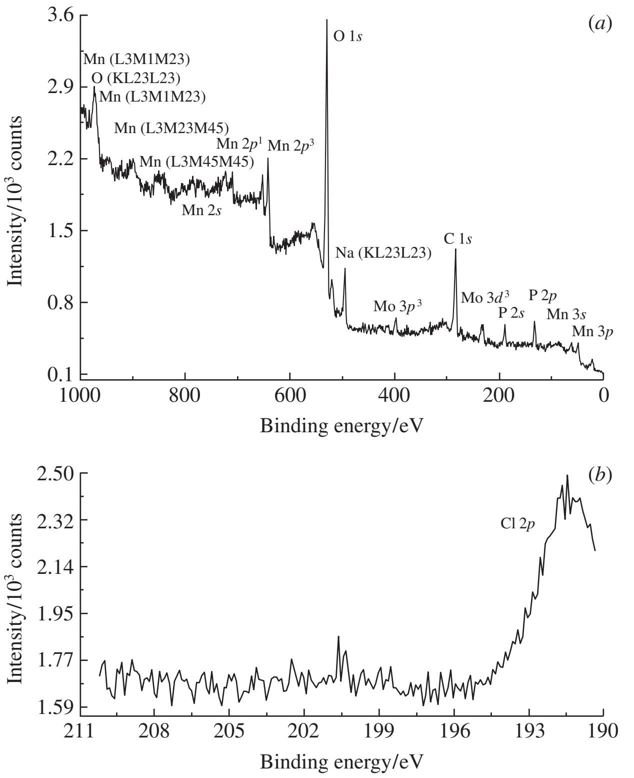

Figure 4 XPS spectra obtained at the $Mn_{1-x}Mo_xO_{2+x}$ electrode surface. Long-time electrolysis (10 h, 0.10 A cm^{-2}) was carried out in buffer solution (pH 8.0): (*a*) overall spectrum and (*b*) Cl2*p* XPS spectrum.

were carried out in phosphate buffer solutions. Phosphate anions can displace Cl^- ions at the electrode surface. A very small amount of phosphorus can be found in the surface layer of $Mn_{1-x}Mo_xO_{2+x}$ (0–1 nm, Figure 4). Nevertheless, the displacement of Cl^- ions by PO_4^{3-} seems unlikely because phosphate ions are only slightly adsorbed at MnO_2 at pH > 7.0.[12]

The manganese content of the surface layer of $Mn_{1-x}Mo_xO_{2+x}$ anodes decreased in the course of prolonged electrolysis in non-buffered NaCl solutions [Figure 2(*a*)]. Such a decrease is caused by the formation of the soluble complexes $Mn(H_2O)_x(OH)_yCl_z^{(4-y-z)}$ and their subsequent removal from the electrode surface. This process leads to progressive anode degradation and sludge formation (MnO_2 as a result of hydrolysis in the bulk of solution). At the same time, these phenomena do not occur in sulfate solutions [Figure 2(*b*)].

No degradation of anodes occurs in buffered solutions at pH 8.0 because Cl^- ions are not adsorbed at the electrode under these conditions (Figure 4). Thus, in the long-time electrolysis of chloride-containing solutions, it is necessary to use buffer solutions to prevent the interaction of Cl^- ions with manganese oxides at electrode surface.

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