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Influence of the oxyanion nature of the electrolyte on the corrosion/passivation behaviour of nickel

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ABSTRACT

The electrochemical behaviour of nickel in the presence of various electrolyte solutions at 0.1 mol/L concentration exhibits a distinction according to the oxyanion nature of the investigated anions. Passivity is achieved with oxyanions whereas it fails with anions not containing oxygen. SIMS and XPS measurements performed from isotopic and non isotopic KNO_3 electrolytes indicate that the oxygen and nitrogen atoms from nitrate oxyanions are incorporated into the passive film during anodic polarization and with evidence of a direct bonding between nitrogen and nickel surface.

1. Introduction

Some previous studies were shown to rationalize the influence of anion specificity on the corrosion/passivation behaviour of some valve metals such as aluminium, titanium and tantalum [1–3]. These metals are characterized by the presence of a natural passive oxide film with a thickness of a few nanometers (2–5 nm typically) which is formed spontaneously when they are exposed to oxidizing media (air, water). The resistance of valve metals against corrosion originates from the propensity of this passive film to regenerate sufficiently quickly and cohesively after an eventual breakdown.

The investigated anions were conveniently distinguished according to the sign of the viscosity *B* coefficient value between the kosmotropes with $B > 0$ and the chaotropes with $B < 0$. Once the hydrated anions are adsorbed on the surface of the passive film, they may be involved in a thinning process of the passive film through the formation of soluble salts or complexes with surface metallic cations. Although this thinning process is challenged with the concomitant pronounced repassivation (regeneration) of valve metals, the chaotrope anions that are able to dehydrate easily can penetrate into the passive film and thus initiate localized corrosion. At the contrary, passivity was found to occur with the kosmotrope anions that tend to preserve their surrounding hydration shell (the energetic dehydration contribution is too unfavourable); so reflecting that in such conditions the thinning process could not overcompensate film regeneration of the valve metals [2].

It seems therefore interesting from a fundamental point of view to investigate whether the previous trends may be applied to other types of metals with different properties.

Owing to its recognized resistance against corrosion, which is a domain of high technological and economical importance, nickel has been used pure or as an alloying element. It has been the subject of a considerable amount of studies concerning its electrochemical behaviour in many electrolytes and at varying pH [4–30], together with the mechanisms of formation of passive films, their nature, structure and properties [31–47]. The thin air-formed passive film on nickel surface is highly defective and may be removed easily. It is not so cohesive and prone to regeneration as that for the valve metals. However according to various anodization treatments and different experimental conditions, the resulting anodic oxide films were found to exhibit excellent resistance to breakdown. Based on these studies, a duplex structure of the passive film is generally proposed with an inner layer of crystalline NiO with a thickness up to 1.2 nm, and an outer layer of amorphous $Ni(OH)_2$ with a thickness up to 0.6 nm [48], although it has been reported that much thicker films may be obtained in specific conditions [34,40].

According to the Pourbaix diagram of nickel [49], this metal is naturally passive when the solution pH is greater than about 8 and its immunity is preserved when the applied electrical potential is lower than its equilibrium potential. When the solution pH is acid, neutral or weakly basic, nickel (Ni) is known to present often an active–passive transition when increasing the electrical poten-

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tial in many electrolyte solutions. After an activation region where the electrical current increases, the current exhibits a maximum (say a peak) before it decreases abruptly to remain nearly constant during a variable range of electrical potential, and it increases finally due to oxygen evolution and/or transpassive metal dissolution [8,13].

In this study, the electrochemical behaviour of nickel in the presence of various electrolytes has been investigated. The results were complemented by SIMS and XPS measurements from non isotopic and isotopic KNO_3 electrolytes to appreciate the eventual incorporation of oxygen and nitrogen atoms into the passive film.

2. Material and methods

All the salts used: sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), potassium iodide (KI), sodium perchlorate ($NaClO_4$), potassium nitrate (KNO_3), sodium thiocyanate (NaSCN), sodium formate ($NaHCO_2$), sodium acetate ($NaCH_3CO_2$), sodium hydrogenophosphate (NaH_2PO_4), sodium sulfate (Na_2SO_4), were analytical grade products manufactured by Prolabo (France) or Sigma–Aldrich (France). Isotopic potassium nitrate ($K^{15}N^{18}O_3$, 15N-98%, 18O-95%) was purchased from Santa Cruz Biotechnology (USA).

Deionized water was taken as a solvent to prepare the electrolyte solutions at 0.1 mol/L concentration. The pH of the electrolyte solutions was measured with an electronic pH-meter (Hanna Instrument). When the pH of the original electrolyte solution was too basic, say around pH 8, droplets of the following acids were added to decrease the pH value of the corresponding electrolyte solution: fluoric acid (HF) solution at 40 wt.% (Prolabo) in the case of NaF electrolyte solution, formic acid (HCO_2H) solution at 98.5 wt.% (Prolabo) in the case of $NaHCO_2$ electrolyte solution, and acetic acid (CH_3CO_2H) solution at 99 wt.% (Prolabo) in the case of $NaCH_3CO_2$ electrolyte solution.

Small nickel plates were cut from a commercial Ni foil (99%, Goodfellow, UK) with a thickness of 0.5 mm to obtain rectangular shape (1.5 cm × 0.8 cm). Before any experiment, the plates were washed in acetone and rinsed with deionized water. Then, the plates were electropolished twice during 2 min in a 57% sulfuric acid solution at a 0.5 A/cm^2 current density. They were finally rinsed with deionized water and dried in air.

The electrochemical experiments were performed with a potentioscan (Radiometer Analytical S.A. Copenhagen, Tacussel DEA 332, potential range 0–8 V) coupled with a digital converter (Radiometer Analytical, IMT 102) and controlled by a PC running the electrochemical software (Radiometer Analytical, VoltaMaster 2). The electrochemical set up was constituted with a nickel plate as the working electrode and a large flat platinum plate as the auxiliary electrode. The plates were immersed at 1 cm depth in 50 mL of the studied solution. A mercurous sulfate electrode (MSE), Hg/$HgSO_4$/K_2SO_4 saturated solution, served as a reference electrode. All the reported potential values refer to this reference electrode.

Linear voltammograms were performed in the range −1 to +1 V/MSE with a 5 mV/s sweep rate under agitation at 200 rpm (magnetic stirrer) of the studied solution. The same device was used for chronoamperometric experiments where the current intensity was recorded as a function of time at an imposed electrical potential.

The voltammograms were performed at ambient temperature and repeated once to confirm the reliability of the electrochemical results.

For the SIMS and XPS measurements, linear voltammograms were performed on nickel plates from −1 to 0.7 V/MSE with a 5 mV/s sweep rate under agitation at 200 rpm (magnetic stirrer) in the studied electrolyte solution. The treated plates were thoroughly rinsed with deionised water and dried in air before they were analysed.

A Cameca IMS 4F6 apparatus was used for SIMS analysis. Sputtering was performed with a 2 keV cesium ion beam. The incident angle of the ion beam was 45° with respect to the sample surface. A square area with a 150 μm edge length was attacked by the beam and the 20% central area of the crater was analyzed. For SIMS analysis, the masses used were 16 (^{16}O), 18 (^{18}O), 72 ($^{58}Ni^{14}N$), 73 ($^{58}Ni^{15}N$). The natural isotopic abundancies are: 0.20% and 0.36% for ^{18}O and ^{15}N respectively [50].

A K-alpha apparatus (Thermo Scientific) was used for XPS analysis. The excitation source is a monochromatic ray Al Kα (1486.6 eV). Binding energies are calibrated with respect to the C—C bond of C 1s at 284.4 eV. Etching was applied during 5 s with an argon ion beam at 1 keV. XPS measurements were first performed with untreated nickel sample that served as a blank of reference for further assignment of the peaks for the treated samples. The peaks corresponding to the binding energies of Ni $2p_{3/2}$ at 852.46 eV (76.48% at.), 856.40 eV (3.43% at.), 858.60 eV (11.94% at.) were detected, together with O 1s at 531.95 eV (8.15% at.).

After the chronoamperometric experiments, a 3CCD digital video camera, Panasonic NV-GS 120 (Crystal Engine), was used to take photographs of the plates.

3. Results and discussion

3.1. Comparative linear voltammograms

The anodic polarization of Ni in the presence of the studied electrolytes is reported in Figs. 1–3. For $NaHCO_2$, $NaCH_3CO_2$ and NaF electrolytes, the pH of the prepared solution is too high so that Ni remains passive: the current density is very low and the active–passive transition (say the peak) is not observed. Indeed when

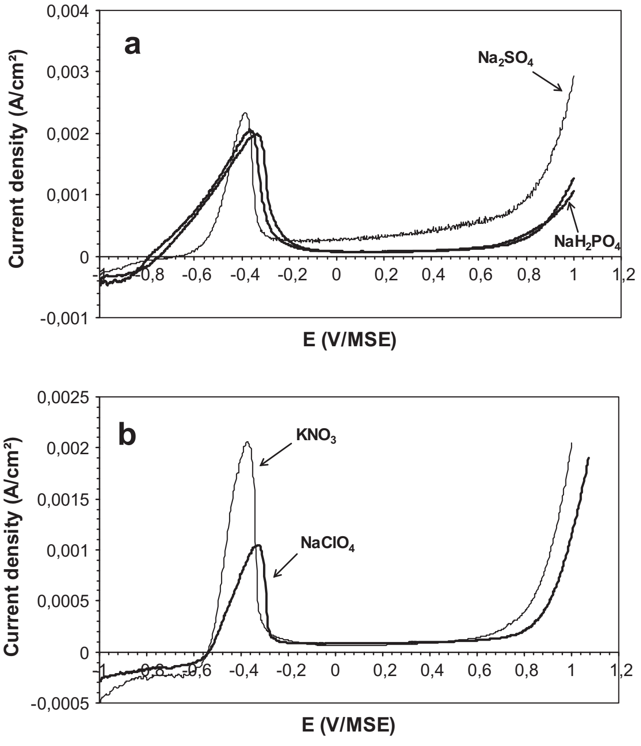

Fig. 1. Linear voltammograms with (a) Na_2SO_4 (thin curve), NaH_2PO_4 (thick curves) electrolytes at 0.1 mol/L concentration and with (b) KNO_3 (thin curve), $NaClO_4$ (thick curve) electrolytes at 0.1 mol/L concentration.