ON THE ELECTROCHEMICAL REDUCTION OF NITRATE ION IN THE PRESENCE OF VARIOUS METAL IONS

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Abstract The role of electrode-inert metal ions (Zr(IV), Hf(IV), La(III), Mg(II), Ca(II), Sr(II), Ba(II) and Li(I)) in electrochemical reduction of nitrate ion is discussed on the basis of polarographic measurement. No evidence for nitrate-metal ion complexes in the bulk solution was found from UV and Raman spectra under our experimental conditions. No large differential capacity (no double-layer effect) which might be assigned to strong adsorption was observed for all the metal ion solutions. However, our results indicated that the metal ion acted as an intermediary for the charge transfer from the electrode to the nitrate ion and as a proton supplier to the nitrate by the hydrolysis of the metal ion itself in the proximity of the electrode.

Key words reduction of nitrate, electrode-inert metal ions, electrochemistry

It is well known that nitrate ion is reduced at mercury electrodes in certain supporting electrolytes[1-3]. However, the reaction kinetics, in particular, the role of the electrode-inert metal ion during the reduction of nitrate have never been made clear. From such viewpoints, we have also investigated[1,2] the electrochemical reduction of nitrate ion in the presence of various metal ions (Zr(IV), Hf(IV), La(III), alkaline earth metal ions, Li(I) and so on) in neutral, weak acidic or basic solutions using polarography, cyclic voltammetry and other techniques.

In this work, we will discuss the role of these metal ions in the reduction of nitrate ion at mercury electrodes, especially the hydrolysis effect of the metal ions[4,5].

EXPERIMENTAL

Analytical-reagent grade chemicals (Wako Pure Chemical Industries, Osaka) were used as received. Using phase-selective ac polarography, the differential capacity was measured and analyzed by the same method as that used by Grahame and Soderberg[6]. The electrochemical and other instrumentation used in this work has been described elsewhere[1,2].

RESULTS AND DISCUSSION

Influence of solution composition on dc polarograms As in Fig. 1, effects of high-valence metal ions on the polarographic wave of the nitrate ion were observed. The nitrate anion is reduced at very negative potentials in a monovalent metal electrolyte. However, the nitrate reduction potential becomes 0.5-1.5 V more positive in the presence of di-, tri- or tetra-valent metal ion than in its absence (in the presence of only 0.1 M LiCl). The dependence of limiting current (i_a) and half-wave potential ($E_{1/2}$) upon the concentration of metal ion ($c(M)$), of nitrate ion ($c(NO_3^-)$) and of proton ($c(H^+)$) was checked for nitrate-tetravalent and -divalent metal ions system[1,2]. These results indicated that 10-50 mM of alkaline earth metal ion and only 0.2 mM of Zr(IV) or Hf(IV) was needed for the reduction of nitrate at a dropping mercury electrode (DME), respectively. However, when

the polarogram of the solution, 1 mM NO_3^- + 0.2 mM Zr(IV) + 45 mM Sr(II) or 33 mM La(III) (pH 2), was recorded, the reduction potential of nitrate was the same as that without Sr(II) or La(III) . This shows that there is no additivity of the electrode-inert metal ions for the reduction potential of nitrate.

Fig. 1. Dc polarograms of nitrate in the presence of various metal ions. (I) 0.1 M LiCl , (II) 50 mM MgCl_2 , (III) 33 mM LaCl_3 , (IV) 0.2 mM ZrOCl_2 + 10 mM HCl + 90 mM LiCl , solid line: $c(\text{NO}_3^-) = 1.0$ mM, dashed line: $c(\text{NO}_3^-) = 0.0$ mM.

When $c(\text{H}^+) > c(\text{NO}_3^-)$, i_a was in proportion to $c(\text{NO}_3^-)$ and $E_{1/2}$ did not change with $c(\text{NO}_3^-)$. On the other hand, when $c(\text{H}^+) < c(\text{NO}_3^-)$, both i_a and $E_{1/2}$ did not change with $c(\text{NO}_3^-)$. However, under the same condition, i_a was in proportion to $c(\text{H}^+)$ and the slope ($dE_{1/2}/dpH$) was positive (120 mV/pH for Zr(IV) and Hf(IV) ; 11 mV/pH for Ba(II) , Ca(II) and Sr(II) ; 53 mV/pH for Mg(II)). The positive slope indicated that the greater the proton concentration, the less the nitrate ion was reducible at DME.

The total reaction The number of electrons in the charge transfer step (n) was determined by controlled potential electrolysis (CPE) as follows: 5.8 ± 0.4 for Zr(IV) [1], 4.9 ± 0.5 for alkaline earth metal ions [2] (cf. 6.1-7.2 for La(III) and Ce(III) [5]). The reduction products were NH_4OH for Zr(IV) (92.4 %) [1] and for alkaline earth metal ions (24 %) [2] (cf. NH_4OH and NH_3 for La(III) and Ce(III) [7]). In general, we can show the reaction equation for the nitrate reduction,

The role of metal ions We have discussed [1,2] the role of metal ions for the electrochemical reduction of nitrate at mercury electrodes as follows: the nitrate-metal ion complexation in the bulk solution, the double-layer effect (the adsorption of the metal ion and/or of the complexion on the electrode before the nitrate reduction), as an intermediary for the charge transfer from the electrode to the nitrate ion, the hydrolysis of metal ion near the electrode [4,5].

No evidence for the complexes in the bulk solution was found under our experimental conditions from UV and Raman spectra. The impedance of the interface between DME and 0.1 M LiCl , 50 mM SrCl_2 , 33 mM LaCl_3 or 0.2 mM ZrOCl_2 + 10 mM HCl + 90 mM NaCl solution was measured in order to obtain the differential capacity by means of phase-selective ac polarography (Fig. 2). However, no large capacity difference which might be assigned to strong adsorption was observed. The differential capacity in the presence of the nitrate ion at more positive potential than that at which the nitrate ion is reduced was the same as that in its absence. We found [1] that there was a linear relationship between the reduction potential of nitrate ion in the presence of various metal ions and the reduction potential of metal ion to the metal. This result indicated that the metal ion acted as an intermediary for the charge transfer from the electrode to the nitrate ion. The positive slope ($dE_{1/2}/dpH$) contradicts the reduction scheme of nitrate, Eq. (1). As in Fig. 3, however, we also found a linear relationship between the reduction potential of nitrate in the presence of various metal ions and the logarithm of the first hydrolysis constant ($\log K_1$) for these metal ions

(M^{x+}) .

Fig. 2. The differential capacity for the solutions of various metal ions. (—) 0.1 M KCl, (----) 0.1 M LiCl, (— — —) 50 mM SrCl₂, (— · — ·) 33 mM LaCl₃, (—●—) 0.2 mM ZrOCl₂ + 10 mM HCl + 90 mM NaCl.

Fig. 3. Relationship between the reduction potential ($E(NO_3^-)$) of nitrate in the presence of metal ion and the logarithm of the first hydrolysis constant ($*K_1$) of the metal ion. (1) Li, (2) Sr, (3) Ca, (4) Mg, (5) Ba, (6) La, (7) Ce, (8) Al, (9) Th, (10) Zr. $E(NO_3^-)$ data from: (6), (7) ref. 8; (8) ref. 9. $*K_1$ data from ref. 10.

The relationship indicates that the easier the metal ion is hydrolyzed, the more the nitrate ion is reducible in the presence of this metal ion. We interpreted these results as indicating that the hydrolysis of metal ion near the electrode supplied protons to the nitrate ion during the electrode reduction. Considering Eq. (1) and the hydrolysis effect of metal ions, we proposed the reduction scheme of nitrate at the electrode,

CONCLUSIONS

We demonstrated that the metal ion had two roles for the reduction of nitrate ion as follows: an intermediary for the charge transfer of the electrode to the nitrate ion, and a proton supplier by the hydrolysis of the metal ion itself near the electrode. These two points explain the reason why the nitrate ion is reduced at more positive potentials (by 1.2-1.5 V) in the presence of a tetravalent metal ion than in the presence of only a univalent cation supporting electrolyte. That is to say, since the tetravalent cation should be reduced at a very positive potential, the tetravalent ion can act as a good intermediary for the charge transfer. Furthermore, since the hydrolysis constant of the tetravalent cation is very large, the cation can be an excellent proton supplier.

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