

SHORT COMMUNICATIONS

Products of Anodic Oxidation of Carbamide: Effect of Temperature

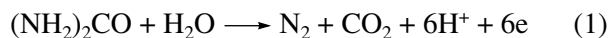
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Received October 9, 2001

Abstract—An unusual (extremum) temperature dependence of current efficiencies for parallel processes of carbamide anodic oxidation in 1 M NaF yielding nitrogen molecules and nitrate is discovered. The temperature effect on the current efficiencies for similar processes in a chloride solution is much weaker.

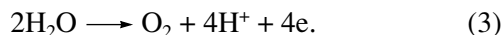
Earlier [1], we noted that the solution composition has a complex effect on the ratio between the rates of anodic processes during the carbamide electrooxidation on a platinum electrode. The anodic oxidation of carbamide proceeds predominantly via two parallel pathways: with the formation of elementary nitrogen



and with the formation of nitrate



In addition, a fraction of the current is consumed by the oxygen evolution process



It was found that the current efficiency for process (1) always increases and that for process (3) decreases with increasing carbamide concentration. At a carbamide concentration in excess of 1 M, process (3) scarcely proceeds. The current efficiency for process (2) passes through a maximum whose location depends on the nature and concentration of supporting electrolyte.

Here, we study the effect of temperature on the current efficiencies for elementary nitrogen evolution and nitrate formation in 1 M NaF and 1 M NaCl. The experimental conditions were similar to those described in [1]. The electrolysis was run in cells with nonseparated anodic and cathodic compartments. A platinum plate with an apparent area of about 1 cm² served as the working electrode. The electrolytes were 0.05–1 M carbamide solutions containing NaF and NaCl. Rates of evolution of anodic gas and carbon dioxide were measured. To do this, the anodic gas was absorbed for a certain time with a Ba(OH)₂ solution, and the weight of the BaCO₃ deposit was determined. To determine the anodic gas evolution rate in the cell with nonseparated electrode compartments, the rate of evolution of all gases formed on both electrodes was measured, and the rate of hydrogen evolution at the cathode was subtracted from it. The hydrogen evolution rate was calculated using the Faraday law. In all cases, the electrolysis

was conducted at a constant current density of 0.1 A/cm². Earlier [2], we found that at 0.1 to 0.2 A/cm², the current efficiencies for processes (1) and (2) were independent of the current density, and at lower current densities (less than 30 mA/cm²), some other processes could proceed (formation of cation radicals with subsequent polymerization or oligomerization), which complicated the situation. The cell temperature was maintained with an U-8 ultrathermostat to within an accuracy of 1°C.

Figure 1 gives plots of current efficiencies for processes (1), (2), and (3) vs. the carbamide concentration in 1 M NaF for 20 and 60°C. As seen, increasing the temperature leads to a relative acceleration of process (1) as compared with process (2), and, at low concentrations of carbamide, also as compared with process (3). At low carbamide concentrations, the current efficiency for reaction (2) is higher than that for reaction (1): with increasing carbamide concentration, this relation changes. The temperature effect on the current efficiencies for processes (1) and (2) in a 1 M carbamide solution (when the contribution of process (3) can be

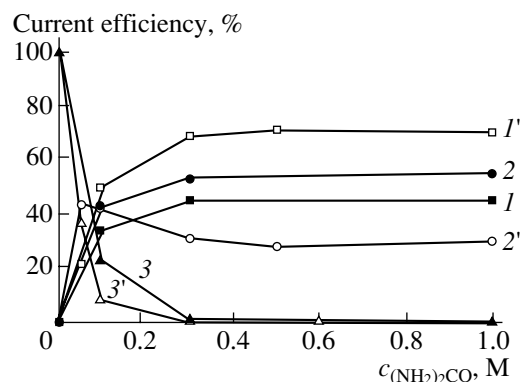


Fig. 1. Plots of current efficiencies for (I, I') nitrogen formation, (2, 2') nitrate formation, and (3, 3') oxygen evolution vs. carbamide concentration in 1 M NaF at (I–3) 20 and (I'–3') 60°C.

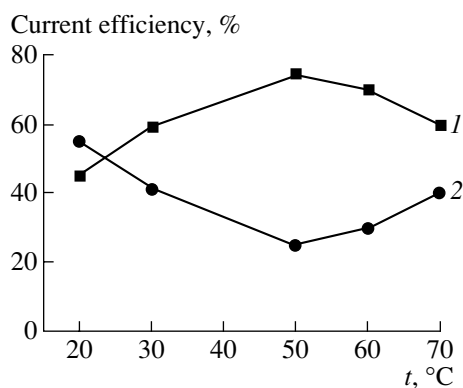


Fig. 2. Temperature dependence of current efficiencies for (1) nitrogen and (2) nitrate formation in 1 M carbamide solutions containing 1 M NaF.

ignored) is rather noticeable and obviously lies beyond the limits of the experimental error.

The data presented in Fig. 1 suggest that the activation energy for process (1), i.e. the carbamide oxidation to elementary nitrogen, is higher than that for process (2), which is a deeper oxidation of carbamide. However, this simple conclusion lacks support from a more comprehensive study of the temperature effect on the current efficiencies for these reactions. Figure 2 gives the temperature dependences of the current efficiencies for processes (1) and (2) in a 1 M carbamide solution containing 1 M NaF throughout the temperature range studied. The extremum character of the curves is in agreement with a complex mechanism of the carbamide electrooxidation. The mechanism involves successive and parallel stages with different activation energies. In this case, varying the temperature can change the limiting stage with a corresponding change in the activation energy for the net process.

The temperature effect on the current efficiencies for individual parallel processes of carbamide elec-

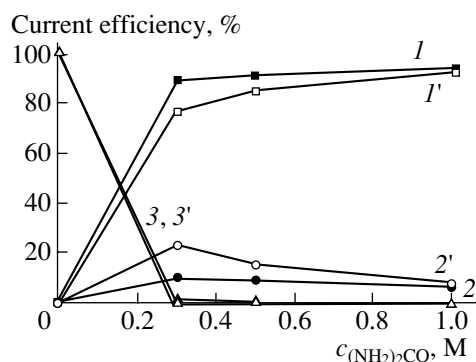


Fig. 3. Plots of current efficiencies for (1, 1') nitrogen formation, (2, 2') nitrate formation, and (3, 3') oxygen evolution vs. carbamide concentration in 1 M NaCl at (1–3) 20 and (1'–3') 60°C.

trooxidation in the chloride solution is significantly weaker. Figure 3 gives relevant data for temperatures of 20 and 60°C. As seen, the temperature effect is commensurate with the error of individual measurements of current efficiencies (5%). This weak temperature dependence (virtually, independence) of the mechanism of the anodic process in the chloride solution is primarily associated with the fact that, in this case, especially at not-too-low carbamide concentrations, the main fraction of the current is consumed by the carbamide oxidation to elementary nitrogen in reaction (1). In such a situation, no unusual effects at other temperatures, similar to an extremum temperature dependence of the current efficiency that was obtained in fluoride solutions (Fig. 2), are to be expected.

REFERENCES

1. Osetrova, N.V. and Skundin, A.M., *Elektrokhimiya*, 2002, vol. 38, p. 304.
2. Osetrova, N.V. and Skundin, A.M., *Elektrokhimiya*, 1994, vol. 30, p. 1257.