

ELECTRO-REDUCTIVE STRIPPING OF VANADIUM IN SOLVENT EXTRACTION PROCESS FOR SEPARATION OF VANADIUM AND MOLYBDENUM

TAKAYUKI HIRAI AND ISAO KOMASAWA

Department of Chemical Engineering, Osaka University, Toyonaka 560

Key Words: Solvent Extraction, Vanadium, Molybdenum, Electrochemical Reduction, Selective Stripping, Separation, Quaternary Ammonium Salt

Introduction

In the previous work, the extraction of vanadium and molybdenum from neutral solution by tri-*n*-octylmethylammonium chloride (TOMAC) and subsequent reductive stripping of vanadium using L-ascorbic acid was investigated.²⁾ It was made clear that the reduction of vanadium was very effective for stripping, with the molybdenum remaining in the organic phase. In this work, the electro-reductive stripping of vanadium from the same metal-loaded organic solution by two-phase electrolysis was investigated.

1. Experimental

The reagents used in this work and the procedure of extraction of vanadium and molybdenum by TOMAC in benzene were the same as described previously.²⁾ The pH 7 aqueous solution containing ca. 0.01 mol/l NaVO_3 and 0.01 mol/l Na_2MoO_4 and benzene solution containing 0.015 mol/l TOMAC were used. The extraction percentages of vanadium and molybdenum were greater than 98% and less than 8%, respectively, and the resulting organic solution contained ca. 9.3×10^{-3} mol/l vanadium and ca. 7.6×10^{-4} mol/l molybdenum. Electro-reductive stripping was carried out using a two-compartment electrochemical cell separated by a cation exchange membrane (Aldrich Nafion 417), as shown in Fig. 1. The working electrode is 12 \times 2 cm platinum mesh (40 mesh). Equal volumes (15 ml) of the organic and aqueous solutions were agitated and electrolyzed in the cathodic compartment. The metal concentration in the aqueous solution was determined by use of an inductively coupled argon plasma atomic-emission spectrophotometer (Nippon Jarrell-Ash ICAP-575 MarkII).

2. Results and Discussion

Since the electrical conductivity of organic benzene solution is too small to reduce the extracted vanadyl ion at the organic phase/electrode interface, cathodic reduction must occur at the aqueous electrolyte/electrode interface in a two-phase electrolysis system, as in the case of uranium reduction.¹⁾ Thus, mass transfer of vanadyl ion from the organic into the aqueous phase should be required. As shown in the previous paper,²⁾ an aqueous solution of pH 2 was suitable for chemical-reductive stripping, since the stripping of molybdenum was minimized at this pH condition. For electro-reductive stripping, however, the pH 2 solution is not suitable, because the mass transfer of vanadyl ion into the aqueous phase and subsequent electrochemical reduction hardly occur. Thus, 0.1

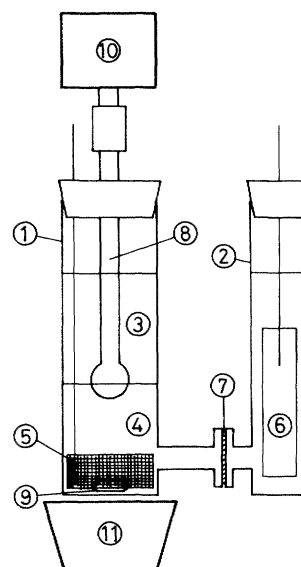


Fig. 1. Two-compartment electrochemical cell for electro-reductive stripping. 1: Cathodic compartment; 2: Anodic compartment; 3: Organic phase (15 ml); 4: Aqueous phase (15 ml); 5: Cathode (platinum mesh); 6: Anode (platinum plate); 7: Cation exchange membrane; 8: Agitator; 9: Stirring bar; 10: Stirring motor; 11: Magnetic stirrer

* Received July 6, 1990. Correspondence concerning this article should be addressed to T. Hirai.

mol/l hydrochloric acid solution was used as the aqueous phase in this study. The stripping yield by contact with this solution at equilibrium (without electrolysis) were ca. 22% and 1.4% for vanadium and molybdenum respectively.

Figure 2 shows the current-voltage curve obtained by using Pt electrodes in the 0.1 mol/l HCl solution containing 0.01 mol/l NaVO_3 . The reduction current of pentavalent vanadium is seen, and it is found that 1.5 V is a suitable electrolysis voltage to reduce the vanadyl ion sufficiently without considerable hydrogen generation.

The relationship between the electrolysis time and stripping yield when both phases are agitated at an agitation speed of 300 rpm is shown in **Fig. 3**. The data at time = 0 show the stripping yield at equilibrium without electrolysis. With the progress of electrolysis, the stripping of vanadium was enhanced and the aqueous phase turned light blue, indicating that the pentavalent vanadyl anion was being reduced to tetravalent VO^{2+} cation. This enabled vanadium to be stripped selectively, as in the case using L-ascorbic acid.²⁾ The stripping percentage of molybdenum was ca. 1% and was not effected by electrolysis.

The agitation speed of both phases significantly influenced the stripping yield. The datum obtained by electrolysis without agitation (only the aqueous phase was stirred by the stirring bar) is also shown in Fig. 3 with the closed key. The stripping of vanadium remarkably decreases, indicating that the mass transfer of vanadyl ion at the organic/aqueous solution interface is the rate-controlling step. Thus, it is expected that the increase in agitation speed brings about the increase in stripping rate. When the organic and aqueous phases are agitated at a speed over 300 rpm, however, the Pt mesh electrode is covered with the organic solution and the electrolytic current is remarkably decreased, since the electrical conductivity of organic benzene solution is extremely small. Thus, in order to obtain a greater stripping percentage and stripping rate of vanadium, the electrochemical cell shown in Fig. 1 should be modified to make agitation stronger.

Conclusion

The electro-reductive stripping of vanadium from benzene solution containing TOMAC was investigated. The pentavalent vanadyl anion was found to be reduced to the tetravalent vanadyl cation at the aqueous electrolyte/Pt electrode interface in the two-phase electrolysis system. This enabled the vanadium to be stripped, while the molybdenum remained in the organic phase. The mass transfer of vanadyl ion from the organic into the aqueous phase was found to be the rate-limiting step; thus the

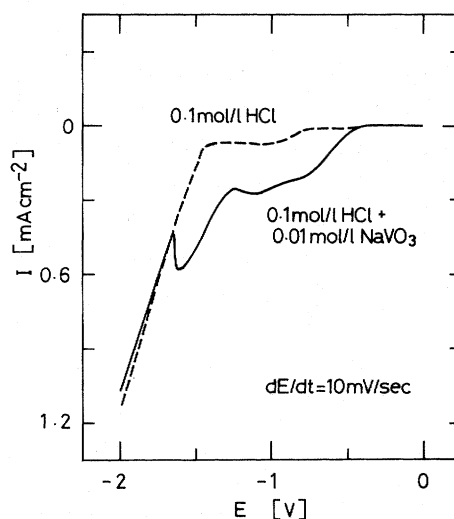


Fig. 2. Current-voltage curve obtained by using platinum electrodes in 0.1 mol/l hydrochloric acid solution containing 0.01 mol/l NaVO_3

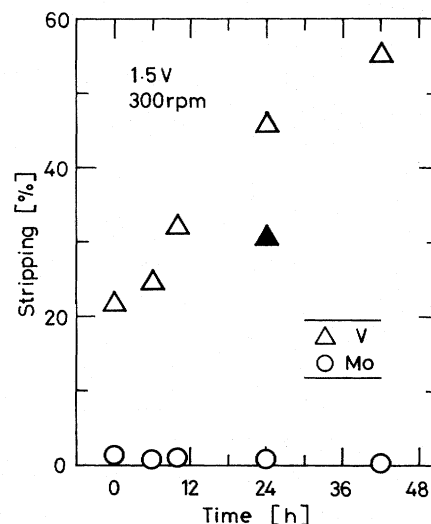


Fig. 3. Effect of electrolysis time on stripping yield of vanadium and molybdenum. Closed key shows a datum obtained by electrolysis without agitation.

agitation speed in both phases influenced the stripping yield and stripping rate of vanadium.

Acknowledgment

One of the authors (T. H.) gratefully acknowledges the financial support of a Grant-in-Aid for Encouragement of Young Scientists (No. 02855236, 1990) from The Ministry of Education, Science and Culture of Japan and a Grant-in-Aid from the Murata Science Foundation.

Literature Cited

- 1) Feess, H. and H. Wendt: *Ger. Chem. Eng.*, **5**, 156 (1982).
- 2) Hirai, T. and I. Komasaawa: *J. Chem. Eng. Japan*, **23**, 208 (1990).