Anodic Behaviour of Vanadium in Alkaline Solutions

Sverre Hornkjøl* and Ingvill M. Hornkjøl

Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway

The anodic behaviour of vanadium has been studied in alkaline aqueous solutions of different compositions. It has been found that vanadium behaves as an active metal in most of the solutions tested, except in the presence of barium ions, where the metal is covered by a thick, non-uniform film containing barium and tetravalent vanadium. True passive behaviour, however, was not found. Correspondingly, the anodic behaviour changed from active to quasi-passive. The results also support previous findings that the dissolution of vanadium goes through an intermediate monovalent state and is catalyzed by hydroxide ions. Some cathodic measurements indicate that the hydrogen evolution is from both the buffer and the water molecules.

During recent years the anodic behaviour of vanadium seems to have been sparsely studied. Its electrochemistry has been surveyed by Kammel and his group,[1] giving data considering general dissolution of and hydrogen evolution on vanadium. In a recent contribution from our laboratory,[2] the anodic behaviour and possible passivation of vanadium in acidic solutions was studied, revealing that passivation could be found in solutions containing barium ions at pH > 4. These studies are extended in the present work to higher pH values and to other alkaline-earth ions. Signs of passivation of vanadium have previously been seen in solutions containing barium nitrate[3] and in glacial acetic acid containing water and sodium borate.[4,5] The aim of the present study has been to elucidate under which conditions vanadium may be passivated and to study the general anodic behaviour of vanadium in alkaline solutions.

Experimental

The experiments were carried out with flag-shaped electrodes (2 cm²) cut from vanadium sheet (99.7 %, Aldrich). The stem of the electrode was lead into a glass tube and sealed with Araldite epoxy resin to avoid problems with the meniscus. The cell was a Pyrex glass cell thermostatted to 25 °C with a separate chamber for the reference electrode (SCE). The auxiliary electrode was a platinum wire immersed directly into the solution through a glass tube. This glass tube partially separated the solution around the platinum wire and the main cell solution without causing a high electrical resistance between the working and auxiliary electrodes.

The solutions were made from AR-grade reagents and water twice distilled in a quartz apparatus. All solutions were deoxygenated by purified nitrogen before and during the measurements. The measurements were performed

both with stagnant solutions and with solutions agitated by nitrogen bubbling. The solution compositions were as follows:

Measurements on active vanadium:

x M CH$_3$COONH$_4$ + (1 − x) M KCl, x = 1, 0.1, 0.01   pH 7

0.50 M NaCl + 0.20 M H$_3$BO$_3$ + 0.10 M Na[B(OH)$_4$]   pH 8.5

0.20 M KHCO$_3$ + 0.20 M K$_2$CO$_3$ pH 10.2

0.10 M Na$_2$HPO$_4$ + 0.30 M Na$_3$PO$_4$ pH 11.5

0.10 M NaOH + 0.90 M CH$_3$COONa   pH 13

1.00 M NaOH   pH 14

Search for passivity:

0.05 M NH$_3$ + 0.05 M NH$_4$ClO$_4$ + 0.10 M NaClO$_4$

or Ba(ClO$_4$)$_2$ pH 9.3

0.002 M NaOH + 0.10 M NaClO$_4$ or Ba(ClO$_4$)$_2$ pH 11.3

0.10 M NaOH + 0.10 M NaClO$_4$ or Ba(ClO$_4$)$_2$ pH 13

0.02 M NH$_3$ + 0.04 M NH$_4$ClO$_4$ + 0.10 M Mg(ClO$_4$)$_2$

or Ca(ClO$_4$)$_2$ or Sr(ClO$_4$)$_2$ or Ba(ClO$_4$)$_2$, all with pH 9.0

The experiments were mostly conducted under galvanostatic control, but potentiostatic control was also occasionally applied, especially in the passivation studies. Active Tafel data were obtained by raising the current density stepwise. For each step 5 min were allowed to elapse before the potential was recorded and a larger current density applied. In the passivation studies the electrode was held at the stabilization potential for 20 h before Tafel data were recorded by potential excursions away from the stabiliza-

---

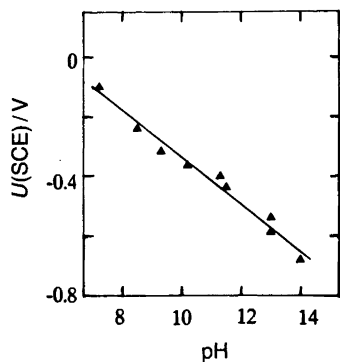* To whom correspondence should be addressed.

Fig. 1. Electrode potential versus pH at $j = 0.42$ A m^{-2} at 25°C, N$_2$ atmosphere and 5 min stabilization time.

tion potential for a few seconds. Between each excursion, the electrode was allowed to regain its original conditions, Capacitance data were always obtained from the initial slope of galvanostatic transients.

Results

Open-circuit data. The extrapolated current densities for anodic dissolution under hydrogen evolution were very small, as they were in acidic solutions.[2] In all the solutions tested, j_{corr} was around 10^{-5} A m^{-2}. The extrapolated corrosion potentials became more negative with increasing pH. However, the scatter in the values was significant, although a slope near -50 mV pH^{-1} seemed to be reasonable. Long extrapolations give rather large uncertainties in both corrosion potentials and dissolution currents, however. These uncertainties probably mask the expected rise in dissolution current density with increasing pH. The directly measured open-circuit potentials were usually about 0.1 V
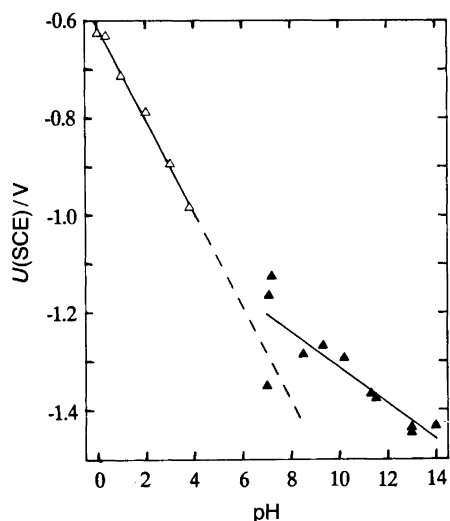

Fig. 3. DC capacitance for V electrodes versus stabilization potential. Data for pH 4.8 are taken from Ref. 2. □, pH 4.8; ▲, pH 7; ◆, pH 8.5; ■, pH 10.2; ●, pH 13. Conditions as in Fig. 1.

more anodic than the extrapolated corrosion potentials, probably owing to traces of oxygen in the cell solution.

Tafel data. Anodic Tafel slopes obtained by galvanostatic measurements were 71 ± 8 mV decade^{-1} for all the solutions. The variation was random with respect to solution composition. This is a much smaller Tafel slope than found in acidic solutions.[2] The cathodic Tafel slope was -140 ± 11 mV decade^{-1}, except in 1.00 M NaOH, where it

Fig. 2. Electrode potential versus pH at $j = -0.42$ A m^{-2}. Conditions as in Fig. 1. At pH 7, the most cathodic potential corresponds to $x = 0.01$, the next to $x = 0.1$ and the most anodic to $x = 1$. Data for the acidic solutions are taken from Ref. 14.
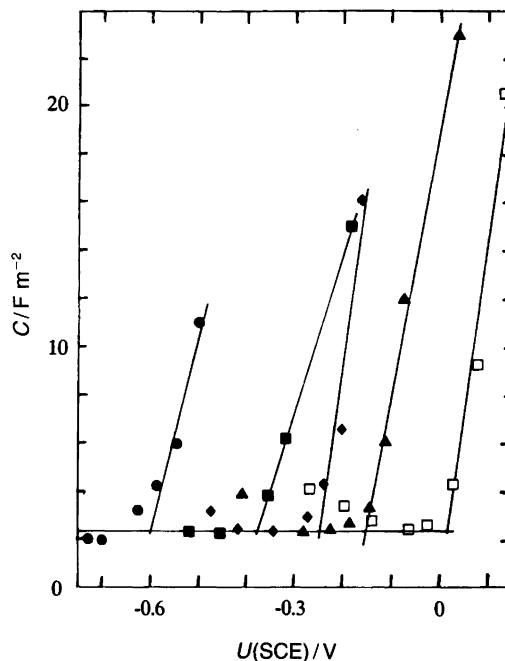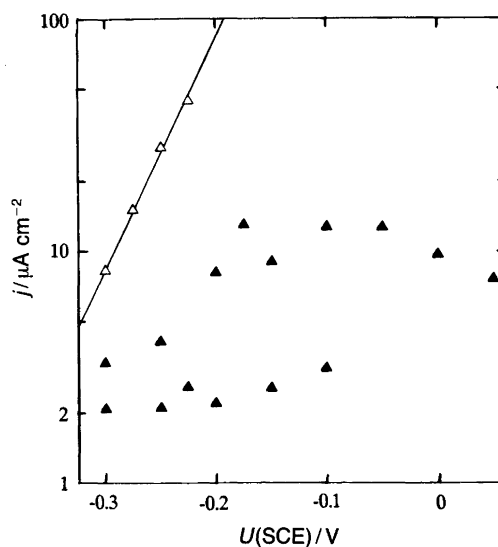

Fig. 4. Anodic current density versus 20 h stabilization potential for quasi-passive V at pH 9. Filled symbols represent the barium solution and open symbols represent the strontium solution. Stagnant solution, 25°C and N$_2$ atmosphere.
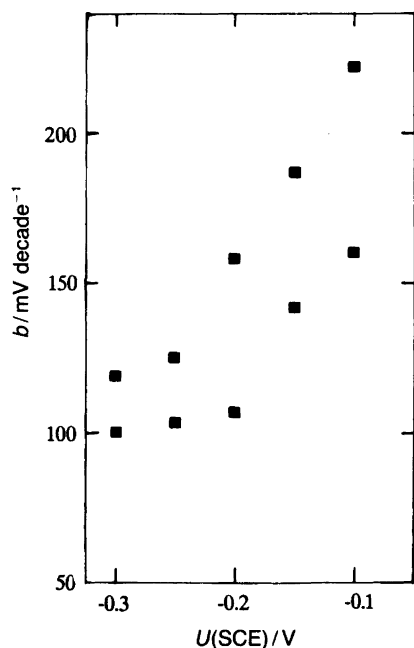
Fig. 5. Initial anodic Tafel slope versus 20 h stabilization potential for quasi-passive V at pH 9, barium-containing solution. Stagnant solution, 25 °C and N_2 atmosphere.

was -95 mV decade^{-1}. The first value is similar to the value found in acidic solutions.[2]

At a constant anodic current density $(0.42$ A m$^{-2})$ the electrode potential decreases at a rate of 79 mV pH^{-1} (Fig. 1). Correspondingly, the cathodic Tafel lines are shifted in the same direction at an average of 36 mV pH^{-1} between pH 7 and 13 (Fig. 2). Superpolarization was only occasionally observed at large current pulses, and stirring effects were negligible.

DC-capacitance data. The electrode capacitance was between 2 and 3 F m^{-2} for all the solutions in the first series, except at the corrosion potential at pH 7.2 (Fig. 3). At a certain potential the capacitance rose sharply. This potential seemed to vary regularly with pH by -75 mV pH^{-1} at pH above 5.[2]

Passivation. Signs of passivation were only observed in solutions containing barium ions. The other alkaline–earth ions gave no signs of introducing passivation. The behaviour in the barium-containing solutions was semi-passive, showing a rather low dissolution current density (Fig. 4), a Tafel slope increasing with the stabilization potential (U'), Fig. 5, and an inverse DC capacitance increasing somewhat with U'. At pH 9, the film was brown-black and contained barium ions and tetravalent vanadium. This was shown by dissolving the film in 3 M HCl and adding a few drops of 3 M H_2SO_4, which gave a blue solution and a white precipitate. The film weighed about 1.3 mg per cm^2 electrode area, which corresponds ot a thickness of about 3 μm.

Discussion

Tafel data. The anodic Tafel slope of 71 mV decade^{-1} supports results obtained previously[1,3,6] for vanadium in alkaline solutions. The shift of the anodic Tafel lines in the cathodic direction with increasing pH in the present alkaline solutions, but not in acidic solutions,[2] indicates that the hydroxide ion plays an important role in the dissolution process in alkaline solutions. Similar behaviour has also been seen for active iron electrodes.[7] From recent modifications of the Butler–Volmer equation one may write eqn. (1) for the anodic Tafel slope,[8] where b_+ is the

$$b_+ = \frac{2.303 \ RT}{n\alpha_+ g \ F} \quad (1)$$

anodic Tafel slope, n is the valence of the metal ion transferred in the dissolution step, α_+ is the anodic transfer coefficient, g is the kink site factor and the other symbols have their usual meaning. With $b_+ = 71$ mV decade^{-1}, one gets $n\alpha_+ g = 0.83$, which is larger than the value found in acidic solutions.[2] The assumption that $g = 2$ would mean that the kink site density rather than diffusion controls the dissolution process. This implies superpolarization and an absence of stirring effects, and the kink density is assumed to change with the current density.[8] However, the actual observation of this superpolarization requires that the change in kink density is not too fast. Accordingly, the present work reports some observations of superpolarization when large current pulses have been applied. The stirring effects observed in the present work have all been negligible, and the assumption of $g = 2$ is therefore considered to be valid, just as in acidic solutions.[2]

It follows that one should have $n\alpha_+ = 0.42$. The transfer coefficient is usually assumed to be near 0.5, and this can only give $n = 1$, meaning that a monovalent step is rate-determining in the dissolution process. Assuming $n = 2$ would only give an extremely unsymmetric reaction, and this assumption is therefore considered invalid. $\alpha_+ = 0.4$ gives a somewhat more symmetric reaction than was found in acidic solutions.[2] If one takes into account that the dissolution reaction seems to be first-order with respect to hydroxide ions, the rate-determining dissolution step could be that of reaction (2). This is similar to what has been suggested previously by Atanasyants and Mavrenkova.[9]

$$V(s) + OH^-(aq) \rightarrow [VOH](aq) + e^- \quad (2)$$
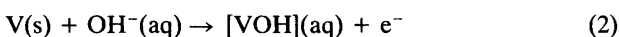
Both the anodic and the cathodic Tafel lines were shifted in cathodic direction with increasing pH, and so also was the corrosion potential. The shift of the cathodic Tafel line (for hydrogen evolution) seems rather surprising, because one should expect that the hydrogen evolution was from water molecules in these alkaline solutions. However, most of the solutions are buffer solutions with rather large concentrations of buffer to maintain a constant pH. The effect of buffer concentration has previously been seen for iron,[10]

and is clearly demonstrated for ammonium acetate solutions around pH 7 (Fig. 2). If one extrapolates the electrode potentials found at $j = -0.42$ A m^{-2} in unbuffered acidic solutions (Fig. 2), the expected electrode potential at pH 7 is in best harmony with the electrode potential found in the solution with low buffer concentration. At pH 13 and 14, which are both unbuffered, essentially the same electrode potential is found.

Capacitance data. The electrode capacitance is more than ten times the Helmholtz capacitance (0.2 F m^{-2} at Hg).[11] A reaction scheme as suggested above will produce a considerable amount of electroactive species at the electrode surface (not only monovalent ones, but di- and trivalent ones too). These electroactive species at the electrode surface would contribute to a large pseudocapacitance, completely covering the pure electrode capacitance. At a certain potential, varying regularly with pH, the capacitance increases sharply, probably due to complete oxidation of all produced species to the pentavalent state. The potential-pH values of the turning points in Fig. 3 all lie inside the domain of pentavalent vanadium in the Pourbaix diagram.[12]

Passivation. For passive electrodes, one should expect a linear relationship between the anodic Tafel slope and the stabilization potential of the electrode.[13] According to Fig. 5, this linear relationship seems very dubious for vanadium in alkaline barium perchlorate solution. An even worse situation is seen for the inverse capacitance versus the stabilization potential. When observing the dried film in an optical microscope, one observes that the film is not covering the metal surface uniformly. From these observations, one can conclude that vanadium does not behave as a true passive metal even in a barium perchlorate solution at pH 9, although the dissolution current density is much lower than without barium ions and the metal is covered by a thick porous film.

References

1. Kammel, R., Kishi, T., Takei, T. and Winterhager, H. *Metalloberfläche 24* (1970) 325.
2. Hornkjøl, S. and Hornkjøl, I. M. *Electrochim. Acta 36* (1991) 577.
3. Bondareva, T. P. *Sb. Nauchn. Rabot. Aspirantov Voronezhsk. Univ. 1962* (1962) 37; *Chem. Abstr. 60* (1964) 12885c.
4. Keil, R. G. and Salomon, R. E. *J. Electrochem. Soc. 112* (1965) 643.
5. Keil, R. G. and Salomon, R. E. *J. Electrochem. Soc. 115* (1968) 628.
6. Shatalov, A. Ya., Bondareva, T. P. and Tsygankova, L. E. *J. Appl. Chem. USSR 36* (1963) 561.
7. Drazic, D. M.: In Conway, B. E., Bockris, J. O'M. and White, R. E., Eds., *Modern Aspects of Electrochemistry*, Plenum Press, New York 1989, Vol. 19, Chap. 2.
8. Wilhelmsen, W. and Hurlen, T. *Electrochim. Acta 32* (1987) 85.
9. Atanasyants, A. G. and Mavrenkova, T. P. *Zh. Fiz. Khim. 50* (1976) 2391; *Chem. Abstr. 86* (1977) 9902d.
10. Hurlen, T., Gunvaldsen, S. and Blaker, F. *Electrochim. Acta 29* (1984) 1163.
11. Delahay, P. *Double Layer and Electrode Kinetics*, Interscience, New York 1965.
12. Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, London 1966, pp. 234–245.
13. Hurlen, T. and Wilhelmsen, W. *Electrochim. Acta 31* (1986) 1139.
14. Fuglevik, I. M. *Elektrokjemisk Oppførsel av Vanadium i Vandige Løsninger*, M. Sc. Thesis, University of Oslo, Oslo 1988 (in Norwegian).