

## O<sub>2</sub> Electroreduction on Ni-Cr-Mo Alloys

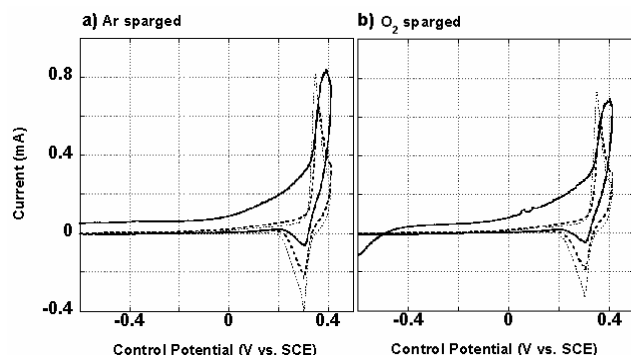
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Oxygen (O<sub>2</sub>) reduction is the most likely process for sustaining metal oxidation in air through electrochemical “local cells” on the metal surface. O<sub>2</sub> reduction occurring at one surface site is the sink for electrons generated during metal oxidation at another. Metal corrosion is reduced when O<sub>2</sub> reduction is slowed or arrested; a process that leads to “cathodic stifling”. O<sub>2</sub> reduction sites become alkaline through the generation of hydroxide. The O<sub>2</sub> reduction of two Ni-Cr-Mo alloys, i.e. C22 and C276 alloys, was studied in a half-cell with aqueous KOH electrolyte to learn the behavior of the O<sub>2</sub> reduction local cells on the passive metal surface. This is to give experimental inputs to computational methods for predicting alloy corrosion. Fresh and aged alloy metal surfaces were studied in alkaline aqueous media with and without nitrate (1M KNO<sub>3</sub>) in the presence and absence of O<sub>2</sub>. Alloy behavior was characterized by electrochemical impedance spectroscopy (EIS) and voltammetry with a still electrode and a rotating ring-disk electrode (RRDE) [1,2]. A spectroscopic graphite rod was the auxiliary electrode, and Saturated Calomel (SCE) was the reference electrode.

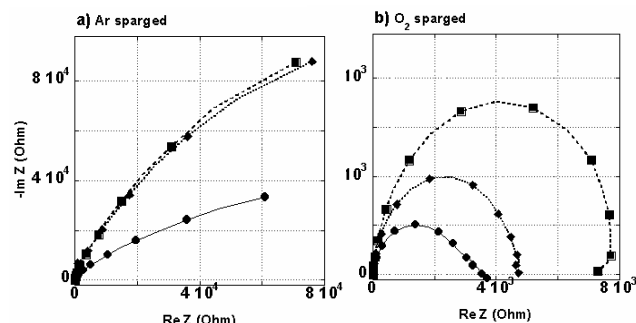
Figures 1a and 1b show typical voltammetry for scans of C22 and similar alloys in alkaline water under Ar and O<sub>2</sub>.



**Figure 1.** Voltammetry of C22 in 1M KOH at 30°C equilibrated with a) Ar and b) O<sub>2</sub>. Area= 1.29 cm<sup>2</sup>. Scan Rate = 10 mV/s. cycle 1 (—); 2 (— —); 3 (····).

The scan profile was similar to that reported by Lloyd, et al. [3] shifted by ~60mV/pH-unit. The range of -600mV to 400mV was chosen based on Jabs et. al. [4] to avoid the transpassive region. The first positive-direction potential scan always showed extra anodic current, indicative of a change in the air-formed, passive film on the metal surface. The oxidation peaked at ~400mV. The first negative-direction scan showed a reduction peak at 350mV. The second and successive cycles showed growing oxidation and reduction peaks shifted to more negative potentials. Under Ar and O<sub>2</sub>, the respective full scan integrals were for: cycle 1 (—) q<sub>ox</sub> = 14.15C; 10.75C and q<sub>red</sub> = 1.33C; 1.04C, cycle 2 (— — —), q<sub>ox</sub> = 5.15C; 4.30C and q<sub>red</sub> = -0.90C; -0.89C, and cycle 3 (····), q<sub>ox</sub> = 5.19C; 4.58C and q<sub>red</sub> = -2.52C; -2.14C. In the positive-direction scans, the integrated current was a smaller value with O<sub>2</sub> present, suggesting a mixed current with O<sub>2</sub> reduction accompanying metal oxidation. In the negative-direction scans, the currents were almost the same under Ar and O<sub>2</sub>, suggesting oxide reduction kinetics are faster than O<sub>2</sub> reduction kinetics. After the second polarization cycle, the cathodic current increased at a greater rate than the anodic current; consistent with a

mixed current during the positive but not negative direction scans. Oxide is accumulating every cycle, but the magnitude of accumulation is decreasing with increasing cycles. Figure 2 shows electrochemical impedance spectra (EIS) for C22 in 1M KOH electrolyte equilibrated with a) Ar and b) O<sub>2</sub> at 30°C scanned from 200kHz to 10mHz with an ac-amplitude of 20mV<sub>pp</sub>.



**Figure 2.** EIS for C22 in a) Ar and b) O<sub>2</sub> sparged 1M KOH at 30°C. The rod was abraded, held at -1.0V for 5min, ramped at 10mV/s to -600mV, aged at -600mV; EIS at -600mV with: ● - 0hr; ■ - 1hr; ◆ -16hr aging. A= 1.29 cm<sup>2</sup>. F = 200 kHz to 10 mHz; ampl. =20mV<sub>pp</sub>.

After the EIS measurements under O<sub>2</sub>, the electrolyte was sparged with Ar for at least 1hr, without removing the rod, and the EIS was repeated. The exception was for no aging at -600mV, where the rod was removed and freshly abraded. Under Ar there is a large ascending arc that does not form a semicircle to 80,000 Ohms. Under O<sub>2</sub>, a full semicircle is seen intercepting the real axis at 3,600, 4,900 and 7,900 Ohm with the electrode held at -600 mV for 0, 16 and 1 hours, respectively. The forming of these 3 semicircles is due to O<sub>2</sub> charge transfer resistance on C22 in this alkaline electrolyte. Apparently metal oxide reduction is slowly occurring at -600mV, resulting in a less resistive oxide film, as the O<sub>2</sub> reduction kinetics actually got faster (semicircle is smaller) after holding at -600 mV for 16 hours compared to 1 hour. Still the smallest semicircle is when there was no aging. In conclusion, the voltammetry under Ar and O<sub>2</sub> suggests accumulation of oxide on C22 and C276 every scan between -0.6 and 0.4 V vs. SCE. O<sub>2</sub> reduction is evidenced by: the suppression of oxidation current in the voltammetry and a full semi circle in the Nyquist plots under oxygen compared to Ar. Additional experiments showed that C276 was similar to C22, except C22 integrated currents were 1C greater than with C276. Nitrate was found to inhibit O<sub>2</sub> reduction on C22 and C276.

## REFERENCES

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## ACKNOWLEDGEMENT

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