### **Transpassive Oxide Films**

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#### Introduction

Metals such as Fe, Al, Ta, Nb and many others cover with thin, dense oxide films in neutral solutions (passivation, formation of e.g.  $Fe_2O_3$  or  $Al_2O_3$ ), which grow according to the high-field mechanism during anodic polarization at high field strengths around  $10^6$  V/cm. This is accompanied by weak corrosion (formation of e.g.  $Fe^{3+}$  or  $Al^{3+}$ ) corresponding to some nA/cm<sup>2</sup>. These oxides are in most cases perfect insulators, only some ionic conductivity is necessary for growths at high field strengths. Some metals (Cr, Fe, Mn, Ni, noble metals), however, develop oxygen as a side reaction,

$$2 H_2 O \rightarrow O_2 + 4 H^+ + 4 e^-$$
 (1)

which becomes dominant at higher potentials around 2 V. This means an additional electronic conductivity, which enables current densities up to some A/cm<sup>2</sup>.

### Transpassivity

The electrodes seemed to be no more passive, and, accordingly, this state was called transpassive. This was sometimes interpreted as at least partial destruction of the oxide film, an idea, which was supported by the acidification (eq. 1) and the formation of an increasing amount of corrosion products with lower valencies (e.g.  $Fe^{2+}$ ). In fact, oxygen evolution is possible only on oxide covered metals.

But this is not the final state. A further increase of current densities means a complete change in mechanism. This starts around  $1 \text{ A/cm}^2$  in bad solvents such as mixtures of highly concentrated perchloric acid, acetic acid and alcohols (used for electropolishing) or in neutral electrolytes (such as NaNO<sub>3</sub> or NaCl, used for Electrochemical Machining) around 5 A/cm<sup>2</sup>. The increasing amount of corrosion products is no more removed by diffusion and supersaturated surface films are formed as most base metal chlorides, nitrates or perchlorates crystallize very slowly, within seconds or days.





Scheme of twin barrelled capillary cell for potentiostatc measurements at 100 A/cm<sup>2</sup>

The properties of these supersaturated films are unique; they are viscous, often intensely coloured, and just in between solutions and melted salts. They can be prepared in macroscopic

amounts and investigated in detail [1]. They are highly soluble in water and, thus, partly dissolved by movement of the electrolyte down to stationary values of some  $\mu$ m. The activity of water is low as almost all water is consumed for hydration of cations and the oxygen evolution is reduced to about 10% of the total charge.

# Experimental

Potentiostatic experiments up to 100 A/cm<sup>2</sup> are challenging. They were realized by capillary cells, which address only  $10^{-3}$  cm<sup>2</sup> and enable such current densities at absolute currents around 1 A. The twin barrelled capillaries (fig. 1) allow strong electrolyte flow up to 10 m/s to remove the products [2], which are identified in special flow-through cuvettes by UV-vis spectroscopy [3] (cations) or by fluorescence quenching of Ru complexes (oxygen, fig. 2) [4]. An example is shown in fig. 3. Altogether, metals such as Al, Ag, Au, Co, Cr, Cu, Fe, Mg, Mn, Mo, Nb, Ni, Ta, Ti, V, W, Zn, Zr and alloys were investigated.





## Results

Oxide films remain on the surface in many cases and are identified by their additional potential drop. They transform in some cases and have again unique properties. They are dissolved into the supersaturated film and are reformed at the metal interface with a stationary thickness of some nm. Most of them enable ionic current densities up to 100 A/cm<sup>2</sup> and electronic current densities up to 20 A/cm<sup>2</sup>.

Four classes of transpassive behaviour were separated [5]:

- formation of high-field oxides, which are identical to common anodic oxides (Al, Ta),
- anion makers, which form anions on top of oxide films (Cr, Mn),
- spinel makers, which form spinel-type oxides whenever possible (Fe, Mn, many alloys, fig. 3),
- weak oxides, which cover only parts of the surface and are easily dissolved (Co, Cu, Mg).



Fig. 3. Current dependent quantitative product analysis for Fe electrodes in NaNO<sub>3</sub>

### References

- 1 M. M. Lohrengel, Chr. Rosenkranz, I. Klüppel, A. Moehring, H. Bettermann, J. Deconinck, B. Van den Bossche, *Electrochim. Acta* 49 (2004) 2863-2870
- 2; M. M. Lohrengel, I. Klüppel, C. Rosenkranz, H. Bettermann, J. W. Schultze, *Electrochim. Acta* 48 (2003) 3203-3211s
- 3 B. Walther, J. Schilm, A. Michaelis, M. M. Lohrengel, Electrochim. Acta 52 (2007) 7732-7737
- 4 C. Hammer, B. Walther, H. Karabulut, M. M. Lohrengel, *J. Solid State Electrochem.* 15 (2011), 1885-1891, DOI 10.1007/s10008-010-1207-5
- 5 M. M. Lohrengel in B. Mollay, M. M. Lohrengel (eds.) "INSECT 2011 Conference Proceedings", Vienna/Wiener Neustadt 2011, ISBN 978-3-00-036247-7