

SUPPLEMENTARY MATERIAL TO

Anodic dissolution of 100Cr6 in nitrate/chloride mixed electrolytes

ANDREAS LESCH, GUNTHER WITTSTOCK, CHRIS BURGER, BENJAMIN WALTHER and JÜRGEN HACKENBERG

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SM-1 Photographs of formed films during LSV in mixed electrolyte at resting disc electrode

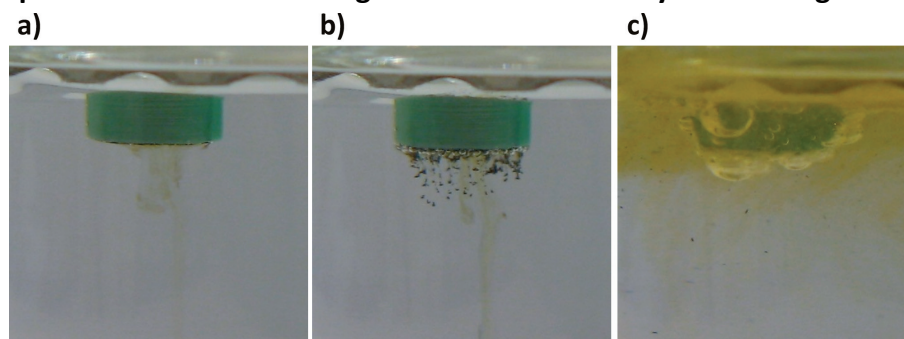


Figure SM-1. Reaction products in mixed electrolytes at static anode; **(a)** green viscous film in section of “chloride curve”; **(b)** Evolution of oxygen after passivation; **(c)** Evolution of oxygen and yellow-green colored solution in section of “nitrate curve”.

Figure SM-1 shows photographs of the transition from active to passive dissolution. During active dissolution the assumed reaction products creep down as a green viscose film (Figure SM-1a). After passivation, the evolution of oxygen breaks off the visible flakes of the black carbide-containing surface layer from the anode surface (Figure SI-1b) and transpassive dissolution can be observed by the formation of oxygen bubbles and yellow-brown colouration of the solution (Figure SM-1c).

SM-2 Programmed Current Chronopotentiometry

Active dissolution in pure NaCl electrolyte and transpassive dissolution in pure NaNO₃ electrolyte are indicated by curves 1 and 7. The PCCs in mixed electrolytes show active dissolution at low current densities. The transition from active to transpassive is indicated by the increase in potential. The current density at transition depends on the relative chloride anion concentration.

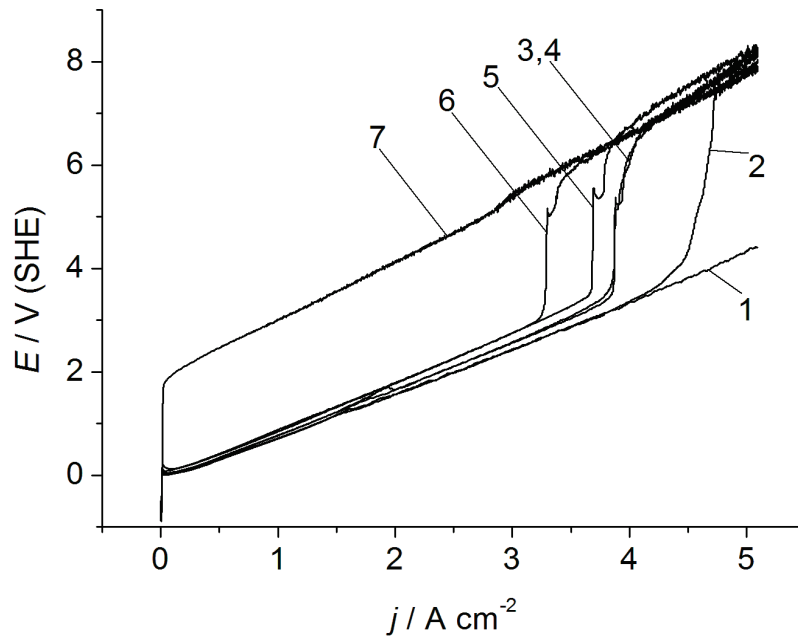


Figure SM-2. PCCs in 3 M NaCl (1), 3 M NaNO₃ (7) and in mixed electrolytes with relative chloride concentrations θ : 0.83 (2), 0.67 (3), 0.5 (4), 0.33 (5), 0.17 (6); rotation rate 3000 rpm; Scan rate 50.9 mA cm⁻² s⁻¹.

SM-3: Correction of current efficiency of inactive carbides

A correction of current efficiency considering the elementary carbon and the metal carbides which are assumed to be electrochemically inert can be done by using the equations SM-3-1 to SM-3-3.

$$m_{\text{inert}} = m_{\text{tot}} \cdot \rho_{\text{C}} \cdot \left(\rho_{\text{C,elementary}} \cdot \frac{M_{\text{C,elementary}}}{M_{\text{C,elementary}}} + \rho_{\text{C,Fe}_3\text{C}} \cdot \frac{M_{\text{Fe}_3\text{C}}}{M_{\text{C,elementary}}} + \rho_{\text{C,Fe}_{2.5}\text{C}} \cdot \frac{M_{\text{Fe}_{2.5}\text{C}}}{M_{\text{C,elementary}}} \right) \quad (1)$$

$$m_{\text{inert}} = m_{\text{tot}} \cdot 0.01 \cdot \left(0.2 \cdot 1 + 0.4 \cdot \frac{179.5457}{12.0107} + 0.4 \cdot \frac{151.6232}{12.0107} \right) = m_{\text{tot}} \cdot 0.1123 \quad (2)$$

$$m_{\text{inert}} = m_{\text{C,elementary}} + m_{\text{Fe}_3\text{C}} + m_{\text{Fe}_{2.5}\text{C}} \quad (3)$$

- m_{inert} – total mass of assumed inert carbon compounds in annealed to globular cementite 100Cr6
- $m_{\text{C,elementary}}$ – mass of elementary carbon
- $m_{\text{Fe}_3\text{C}}$ – mass of Fe₃C
- $m_{\text{Fe}_{2.5}\text{C}}$ – mass of Fe_{2.5}C
- m_{tot} – experimental weight mass loss of annealed to globular cementite 100Cr6 specimen
- ρ_{C} – weight percentage of total carbon in 100Cr6
- $\rho_{\text{C,elementary}}$ – percentage of elementary carbon of total carbon
- $M_{\text{C,elementary}}$ – molar mass of carbon
- $\rho_{\text{C,Fe}_3\text{C}}$ – percentage of carbon, bound in Fe₃C, of total carbon
- $M_{\text{Fe}_3\text{C}}$ – molar mass of Fe₃C
- $\rho_{\text{C,Fe}_{2.5}\text{C}}$ – percentage of carbon, bound in of Fe_{2.5}C, of total carbon
- $M_{\text{Fe}_{2.5}\text{C}}$ – molar mass of Fe_{2.5}C