Electrochemical behaviour of Fe and Fe-Si electrodes
in molten hydroxides mixture

Lucia Hrnčiariková, Ján Híveš, Kamil Kerekeš, Ján Kamenár, Miroslav Gál[1]

Department of Inorganic Technology, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia
[1]Department of Molecular Electrochemistry, J. Heyrovský Institute of Physical Chemistry of the ASCR, Dolejškova 2155/3, 182 23 Prague, Czech Republic

jan.hives@stuba.sk

Abstract

Mixture of NaOH-KOH eutectic melt was selected as the most appropriate system for the electrochemical synthesis of Ferrate(VI) in a molten salt at the temperatures of 170 °C. Cyclic voltammetry was used to characterise the processes taking place on the stationary iron and Si-rich iron electrode. The anodic current peaks corresponding to the Ferrate(VI) production as well as cathodic current peaks corresponding to the Ferrate(VI) reduction appeared on voltammetric curves. EIS method was used to characterise surface layers on the anode materials during Ferrate(VI) preparation. Impedance spectra are characterised with two time constants which correspond to the model of duplex layer structure on the anode surfaces.

Keywords: Ferrate(VI), Molten Hydroxides Mixture, Electrochemical Impedance Spectroscopy, Cyclic Voltammetry

Introduction

The electrochemical way of Ferrate(VI) production provides product of high purity. The synthesis of Ferrate(VI) by an anodic dissolution of metallic iron proceeds typically in the transpassive potential region. At these conditions, the surface of the iron anode is covered by a partly disintegrated (e.g. containing cracks and/or pores) oxo-hydroxide layer. Efficiency of the synthesis is strongly influenced by the protective properties of this layer. These can be affected into a significant degree by the anode material used and/or by the reaction conditions, i.e. by the electrolyte concentration, composition, temperature and the cell arrangement (Híveš et al. 2008).

Preparation of Ferrate(VI) by anodic polarisation of iron electrode in the molten hydroxide possesses important advantages when compared to the classical electrolysis in the water solution environment. First, there is an absence of water in the system, which is an advantage since water decomposes Ferrate(VI). Further on, passivation properties of the iron anode are strongly reduced in molten salt environment. This approach represents an interesting challenge, which may open a new way of Ferrate(VI) production.

Experimental

The eutectic mixture of NaOH and KOH was used (51.5 mol. % NaOH) as an electrolyte in this case. The NaOH and KOH solids (p.a. grade, MikroCHEM, Slovak Republic) were vacuum-dried in an oven over P_2O_5 for five days at a temperature gradually increasing up to 200 °C. The differential temperature analysis (DTA) and thermal gravimetry (TG) showed a presence of ~1.5 mol. % water in the hydroxides treated in this way. 60 g of the eutectic mixture at 170 ºC was used as the electrolyte. The temperature of the molten mixture was measured using a Pt-Pt10Rh thermocouple. All experiments were carried out in a stationary three-electrode arrangement. The cell consisted of a PTFE crucible immersed in oil bath with temperature control ±0.1 ºC. The working electrode (WE) in the form of a sheet was made of pure iron (99.95 wt. %) and iron material with a small Si content (3.17 wt. % Si). Geometric surface area of WE was about 0.36 cm^2. The quasi-reference electrode (RE) was made of pure iron. The same material was used also for counter electrode (CE). A more detailed characterisation of the kinetics of the electrode processes taking place in the molten salt environment was provided. In the first step, cyclic voltammetry (CV) was used to identify the basic electrochemical characteristics of the system. The properties of the layers covering the surface of the iron electrode during the steady anodic polarization were quantified in the second step by means of electrochemical impedance spectroscopy (EIS). Both the CV and EIS measurements were carried out using an AUTOLAB Electrochemistry System (ECO Chemie, Netherland). Prior to each EIS experiment the electrode was polarised anodically at the given experimental potential for 2 minutes in order to reach quasi-steady state conditions. After an initial delay, the impedance spectrum was recorded in the frequency range of 10 Hz to 100 kHz using a perturbation signal with amplitude of 5 mV, 61 experimental points were taken within measured frequency range. Fig. 1 represents schematic drawings of the measuring apparatus.
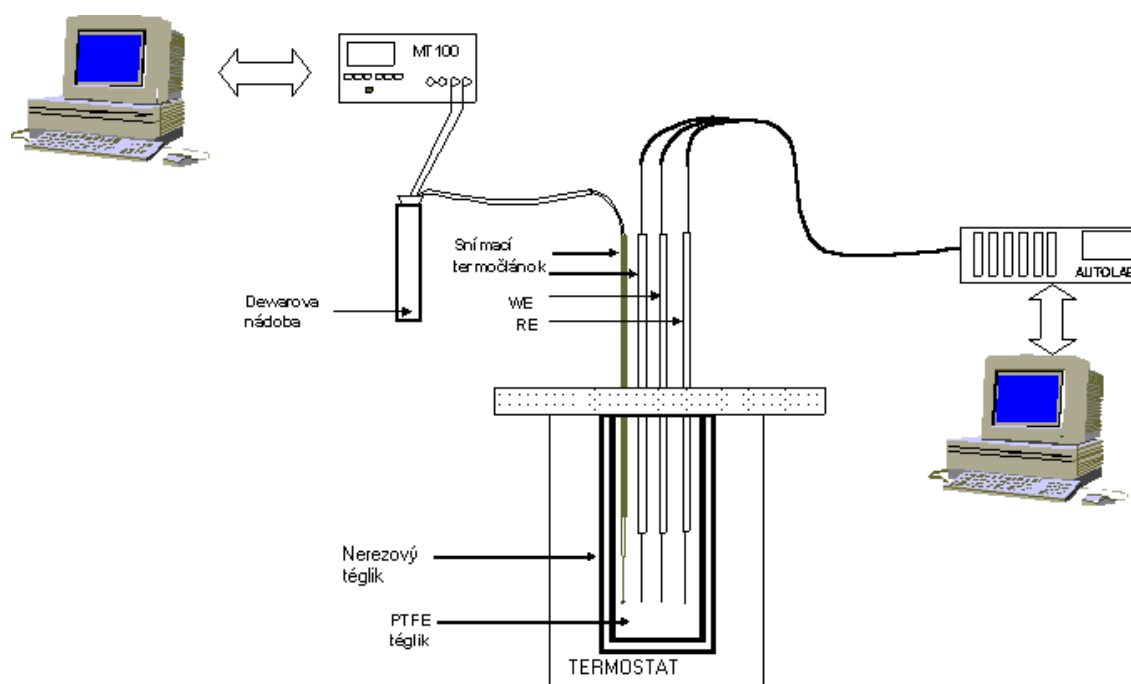
Fig. 1. Experimental apparatus.

Results and Discussion

Cyclic voltammetry

Typical polarization curve of the iron and Si-rich iron electrode in the molten eutectic NaOH-KOH mixture at the temperatures of 170 °C is shown in Figs. 2-3.

It is clearly seen, that the highest anodic peak of current density is obtained in the potential region ~0.150 V. It corresponds to the active iron dissolution according to Eqn.(1).

$$Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e^- \tag{1}$$

The last anodic peak (Figs 2-3) in the potential region ~1.590 V is well distinguishable on the polarisation curve. The peak was identified to correspond to the ferrate production according to one or more of Eqs.(2–4).
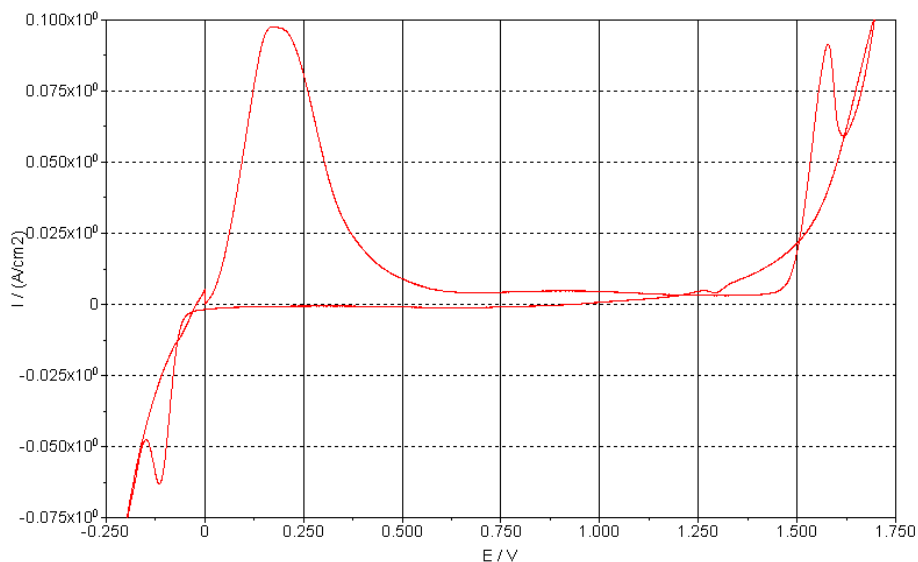
$$Fe(OH)_3 + 5OH^- \rightarrow FeO_4^{2-} + 4H_2O + 3e^- \tag{2}$$

$$Fe_2O_3 + 10OH^- \rightarrow 2FeO_4^{2-} + 5H_2O + 6e^- \tag{3}$$

$$FeO_2^- + 4OH^- \rightarrow FeO_4^{2-} + 2H_2O + 3e^- \tag{4}$$

Fig. 2. Cyclic voltammogram of the iron electrode in the eutectic NaOH-KOH molten system at 170 °C. Potential scan rate 200 mV s^{-1}.
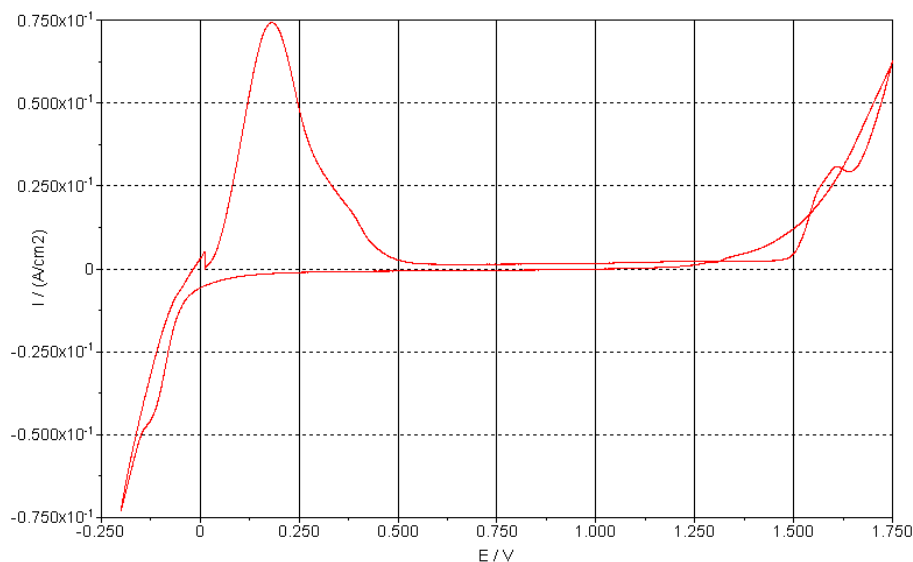

Fig. 3. Cyclic voltammogram of the Fe-Si electrode in the eutectic NaOH-KOH molten system at 170 °C. Potential scan rate 200 mV s^{-1}.

In Fig. 2 the ferrate reduction peak is also clearly seen at the potential of about 1.300 V. Potential shift between Ferrate(VI) oxidation peak and Ferrate(VI) reduction peak is

approximately 300 mV. This difference is much smaller compared to a similar reaction in the aqueous environment (900 mV) (Híveš et al. 2008). This result clearly indicates that the anode surface in molten electrolyte is significantly more electrochemically active as in aqueous solution. The only explanation for such a situation is that the electrode surface is, to a significant degree, free of passivating oxo-hydroxide films. These are typically formed in a potential region of passivity or prolonged polarisation at the transpassive potentials in the aqueous environment. The results obtained indicate that the situation differs in the case of the molten salt environment. Here the passivating surface layer is probably completely removed by the reaction with the chemically aggressive molten salt environment.

The cyclic voltammetric curves at different scan rates for measured electrode materials are shown in Figs. 4-5.
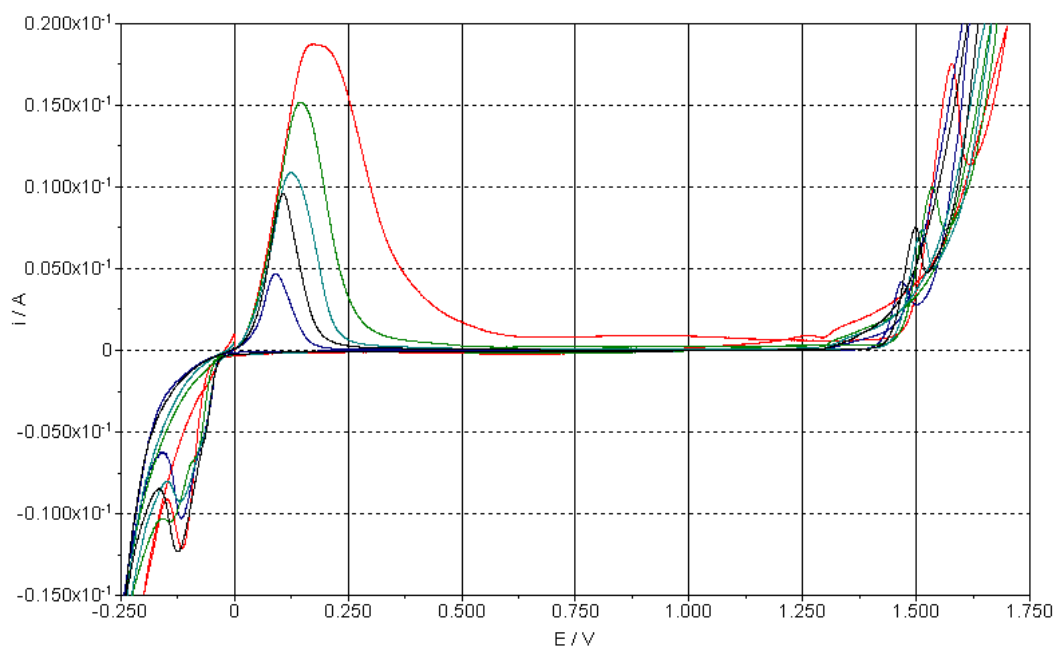

Fig. 4. Cyclic voltammograms of the iron electrode in the eutectic NaOH-KOH molten system at 170 °C. Potential scan rate 4, 10, 20, 50, 200 mV s^{-1}.
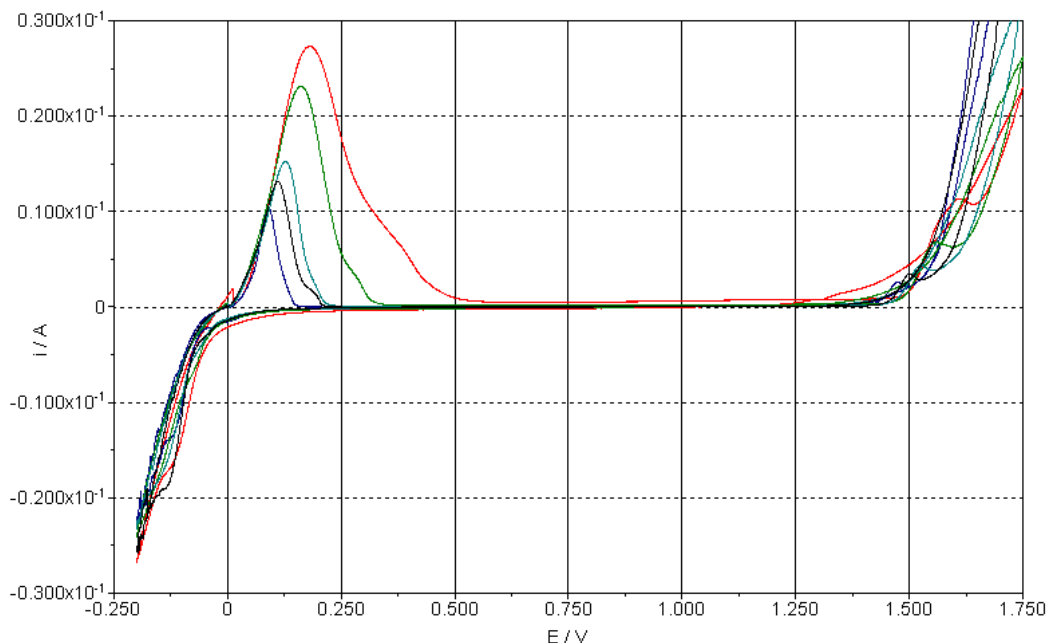
Fig. 5. Cyclic voltammograms of the Si-rich iron electrode in the eutectic NaOH-KOH molten system at 170 °C. Potential scan rate 4, 10, 20, 50, 200 mV s^{-1}.

Electrochemical Impedance Spectroscopy

EIS allows a more detailed characterisation of the anode surface processes and especially of the surface layers. Measured impedance spectra are characterised by two time constants (Fig. 6 and 7). The reactions at the iron electrode in molten salts are rather complicated and there is no generally accepted reaction mechanism of Ferrate(VI) formation. Its exact mathematical description seems to be not possible. For this reason we used an alternative approach using the equivalent circuit method (Fig. 8). As was shown previously, the application of a physical model of a sandwich-type surface layer represents an optimal solution (Bouzek and Bergmann 1999). The correctness of such a model was proved experimentally by means of Mössbauer spectroscopy (Bouzek and Nejezchleba 1999). The two parallel R-CPE components correspond to the two sublayers covering the /anode surface, which differ in the protective properties and composition. They are connected in series with an electrolyte resistance and outer inductance. A Constant Phase Element (CPE) has been used instead of capacitance in order to describe the nonideality of the system studied. The results of nonlinear regression analysis of impedance spectra confirmed that the decrease in surface film resistivity with increasing potential is related to the breakdown of its compact structure and thus its protective properties.
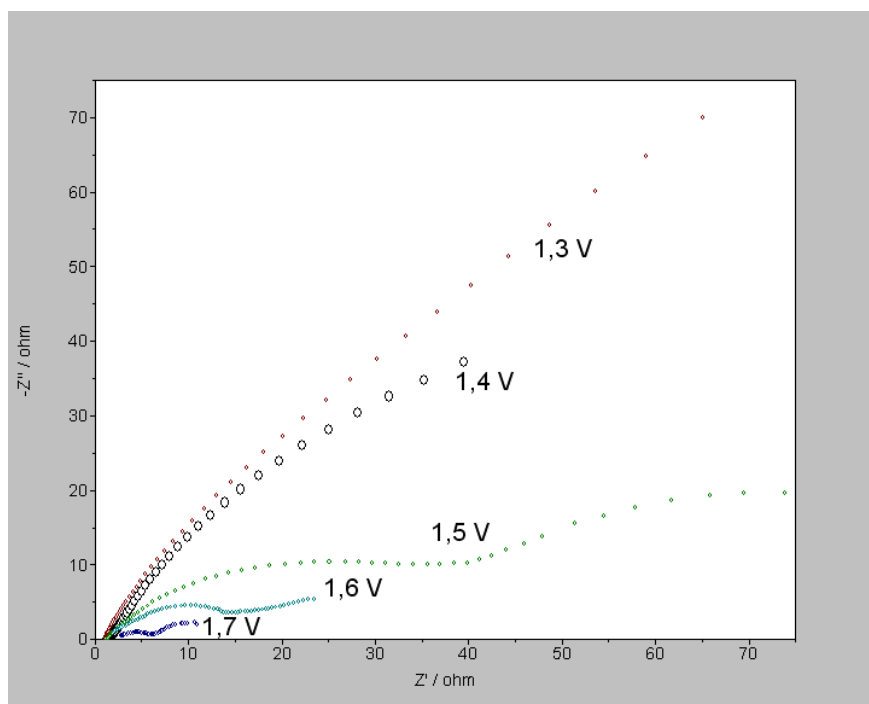
Fig. 6. Nyquist plots of impedance spectra obtained in the eutectic NaOH-KOH molten system at 170 °C for various potentials (Fe-Si working electrode).
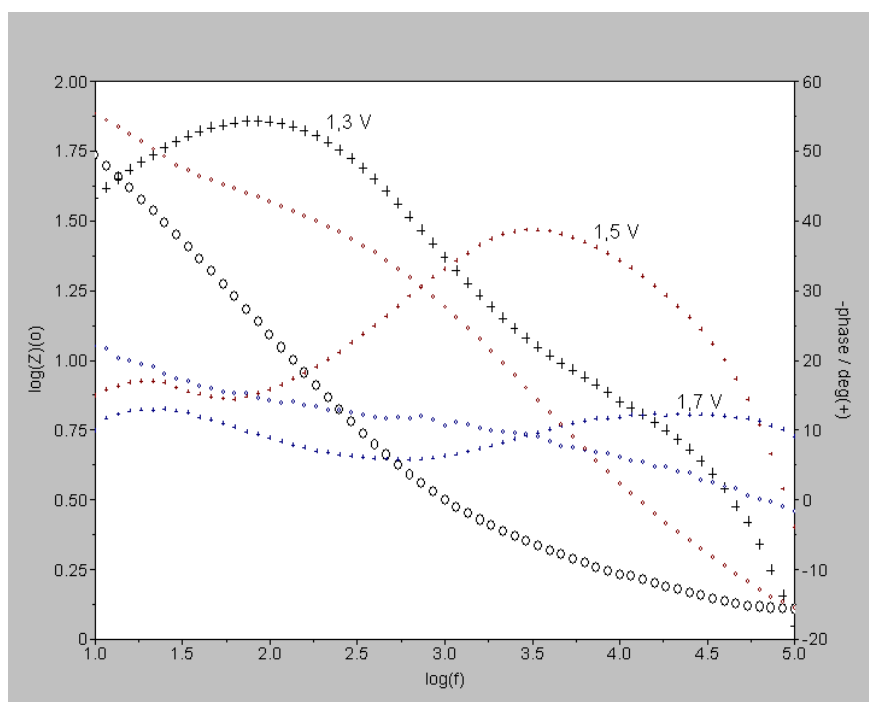

Fig. 7. Bode plots of impedance spectra obtained in the eutectic NaOH-KOH molten system at 170 °C for various potentials (Fe-Si working electrode).
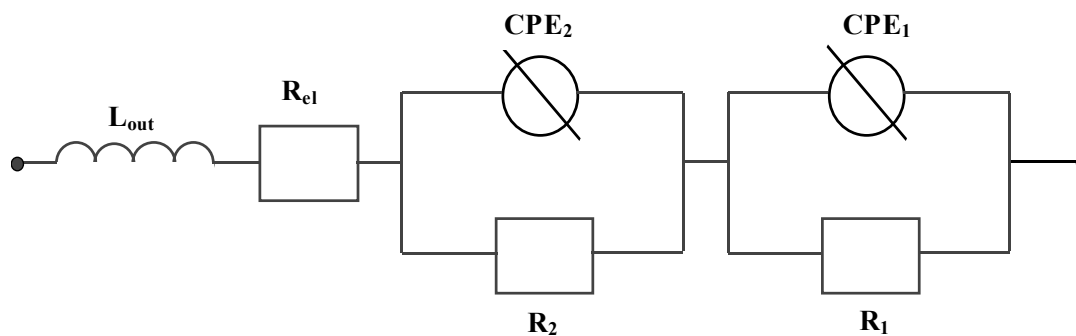
Fig. 8. Equivalent circuit used for non-linear regression analysis.

Resistance value of inner-passive layer has value of hundreds of Ω at the beginning of Ferrate(VI) generation area. By increasing polarization these values rapidly decrease to value of 1 Ω. Low value is evidence of protective passive layer disintegration at the both cases. At the beginning, the capacity of inner layer increases and its value is changing in a range of several orders. In the region of high potentials the capacity of inner layer decreases back to a few μF units, which is the evidence of disintegration of the layer adjacent to the iron electrode. The capacity of the inner layer at the temperature of 170 ºC increases with the polarization of Fe-Si electrode. In the plateau region on the polarization curve the capacity of the inner layer exhibited a stable value (cca 150 μF).

Resistance value of the outer-passive layer rapidly decreases for both electrode materials with increasing anodic polarisation. Resistance value of the outer layer decreases from 135 Ω to 0,4 Ω at the potential of 1,6 V. Initially the capacity increases (from 6 to 180 μF) and then with increasing polarization decreases to a few units of μF values. This also proves the disintegration of the layer at higher polarization potential values.

This view is also supported by the comparison of these results with the potentiostatic polarization curves shown in Fig. 9. The decrease in surface film resistivity occurring in two steps corresponds well with the occurrence of the Ferrate(VI) formation plateau and commencement of oxygen evolution on the polarization curve.
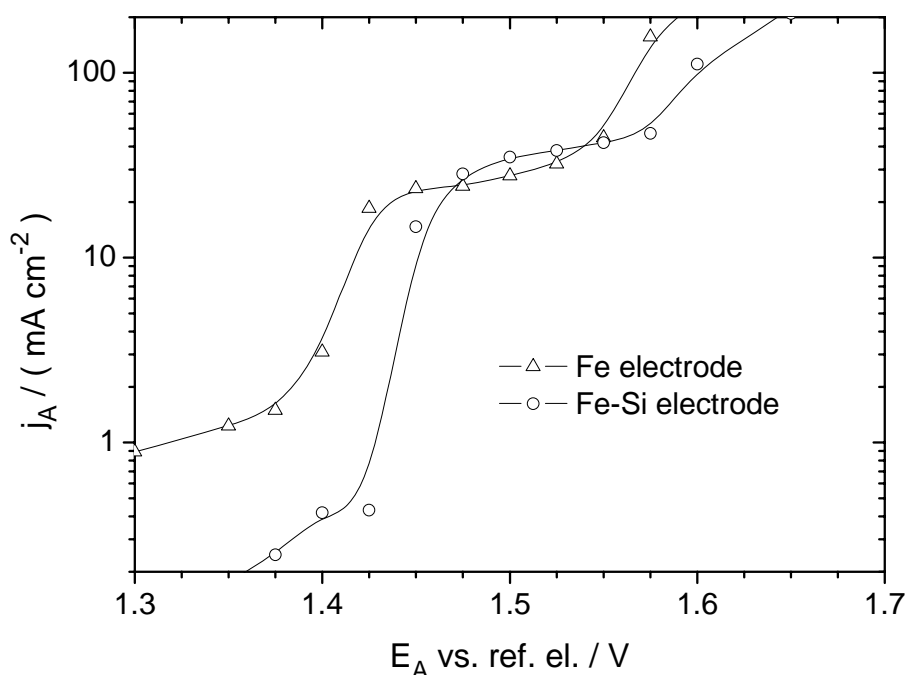
Fig. 9. Potentiostatic polarisation curves of the Fe and Fe-Si electrode in eutectic NaOH-KOH molten system at 170 °C obtained from the EIS measurements.

Conclusions

The results of CV and EIS experiments indicate a significant increase in the aggressiveness of the molten salt environment with respect to the aqueous solution. This is manifested in the change of cyclic voltammograms. In molten electrolyte the passivation of the electrode surface in the transpassive potential region is less progressive. This conclusion was confirmed by the a high electrocatalytic activity of the electrode surface indicated by the shift of the Ferrate(VI) reduction potential to less anodic values. The CV results further stress the importance of the operational temperature with respect to the stability of the Ferrate(VI) as a product. Its lifetime at the temperature of 170 °C was assessed as units of seconds. The results of CV were confirmed by means of EIS indicating a disappearance of the protective surface sublayer in the molten salt environment. The results of nonlinear regression analysis of impedance spectra confirmed that the decrease in surface film resistivity with increasing potential is related to the breakdown of its compact structure and thus its protective properties.

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