



# Influence of additives on the transpassive dissolution of ferritic steels in phosphoric acid - acetic acid electrolytes

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# Outline

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# *Introduction*

- **Electropolishing of steels used in many industrial applications.**
- **Formulation of electropolishing electrolytes from theoretical principles not yet possible.**
- **A need to rationalise electrochemical data relevant to surface leveling exists.**



# Aim of the work

- **To investigate the transpassive dissolution of industrial ferritic steels in phosphoric-acetic acid mixtures by electrochemical methods**
- **To verify the applicability of a previously proposed kinetic model to the experimental results and to estimate the values of the kinetic parameters**

# Experimental

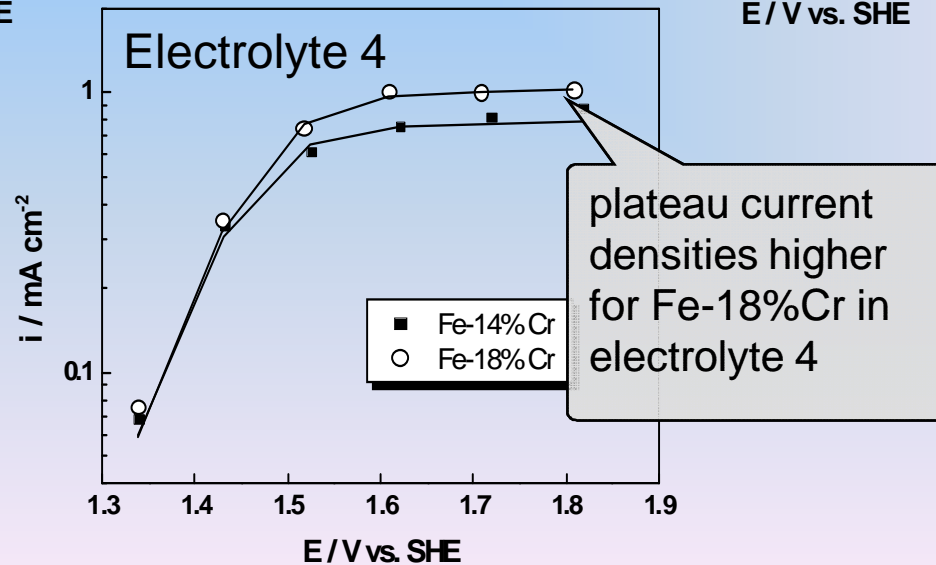
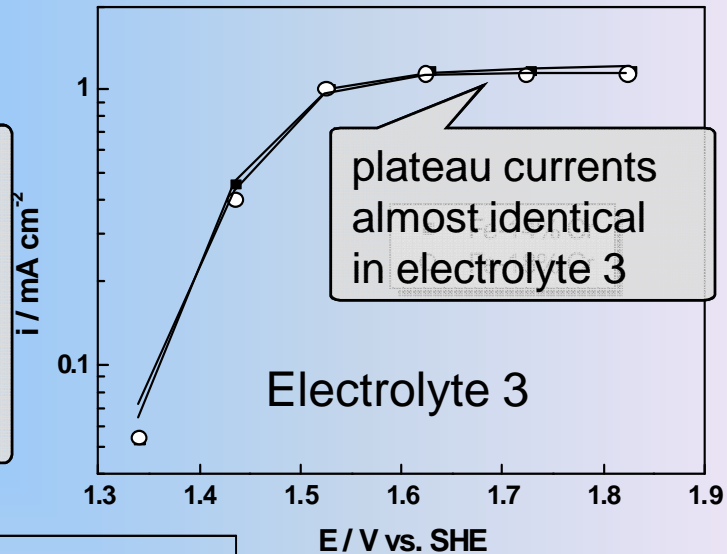
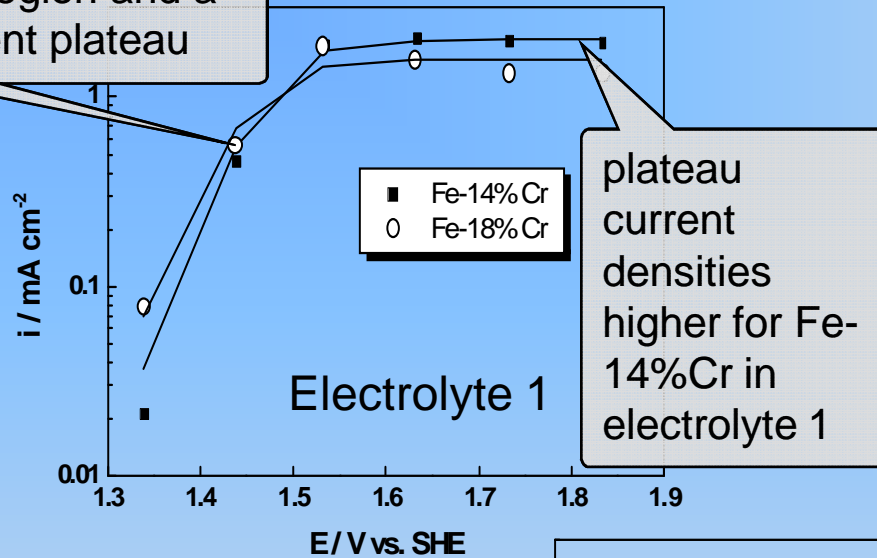
- Industrial ferritic steels (14% and 18%Cr) used as working electrodes
- Experiments carried out at  $20 \pm 1$  °C in naturally aerated solutions
- Voltammetric and impedance measurements – Autolab PGSTAT 30 + FRA module
- Fit and simulation – Maple 8.1 and Microcal Origin 6.0

Electrolyte No.	Composition of the electrolyte
1	13.5M $\text{H}_3\text{PO}_4$ - 0.5 M $\text{H}_2\text{SO}_4$ - 2 M $\text{C}_3\text{H}_5(\text{OH})_3$
2	13.5M $\text{H}_3\text{PO}_4$ - 0.5 M $\text{H}_2\text{SO}_4$ - 3 M $\text{C}_3\text{H}_5(\text{OH})_3$
3	7.5 M $\text{H}_3\text{PO}_4$ - 7.5 M $\text{CH}_3\text{COOH}$ - 0.5 M $\text{H}_2\text{SO}_4$ - 2 M $\text{C}_3\text{H}_5(\text{OH})_3$
4	1.5 M $\text{H}_3\text{PO}_4$ - 7.5 M $\text{CH}_3\text{COOH}$ - 0.5 M $\text{H}_2\text{SO}_4$ - 2 M $\text{C}_3\text{H}_5(\text{OH})_3$



# Results – steady state

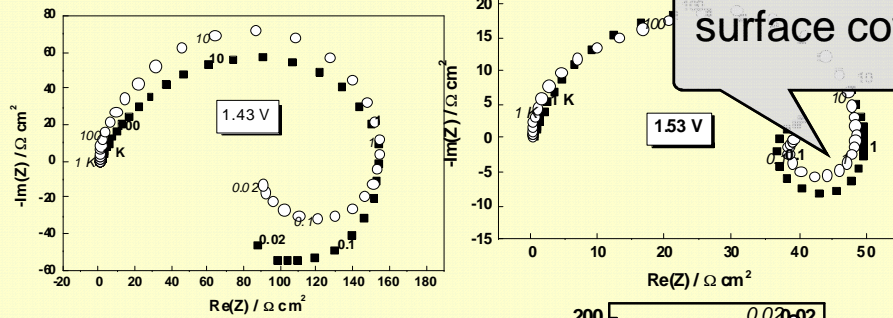
The curves comprise a Tafel-like region and a current plateau



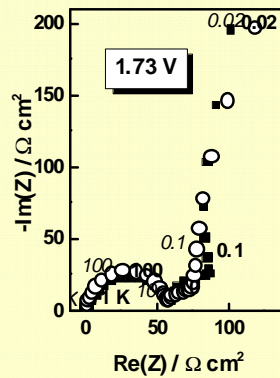
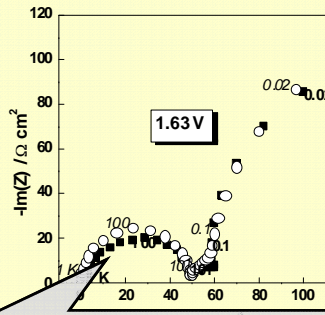
# Results impedance

## Electrolyte 1

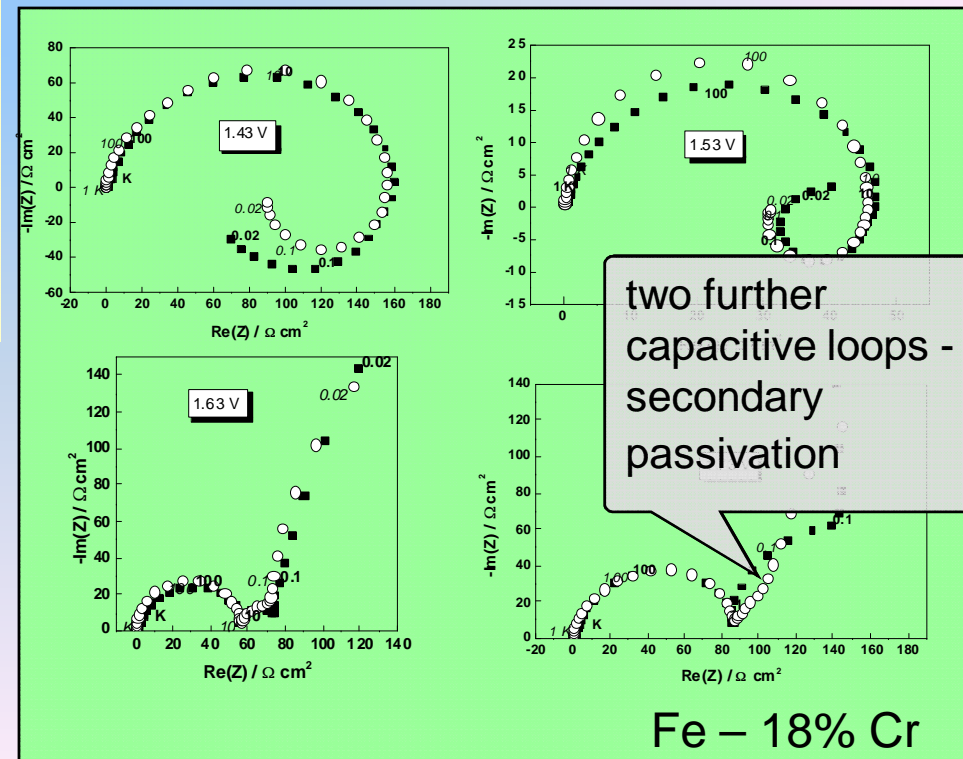
Fe – 14% Cr



low-frequency inductive loop - relaxation of surface coverage



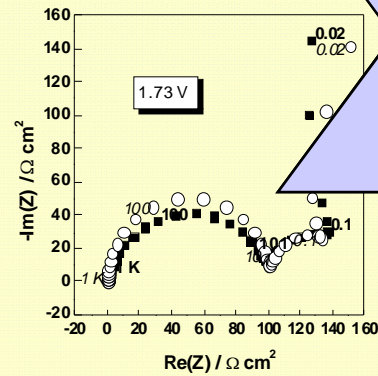
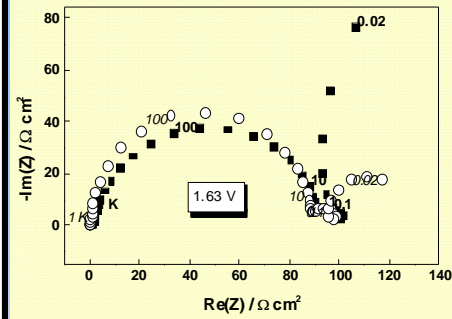
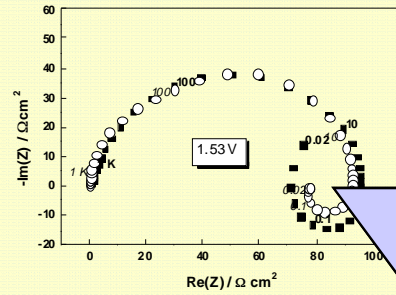
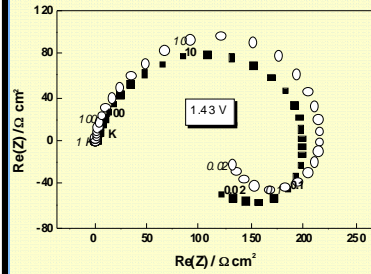
high-frequency loop - charge transfer



two further capacitive loops - secondary passivation

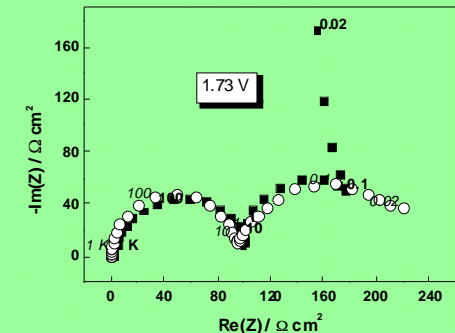
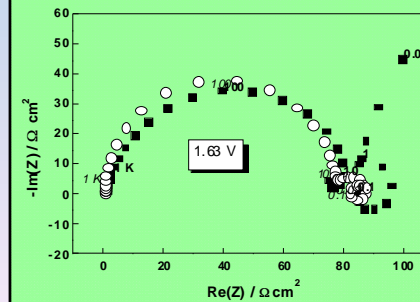
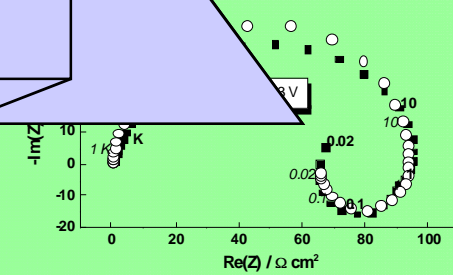
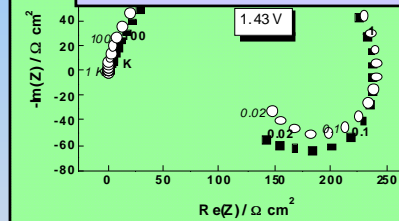
Fe – 18% Cr

## Fe – 14% Cr



## Electrolyte 3

impedance at low frequencies in electrolytes 1 and 3 lower for Fe-14%Cr – surface leveling



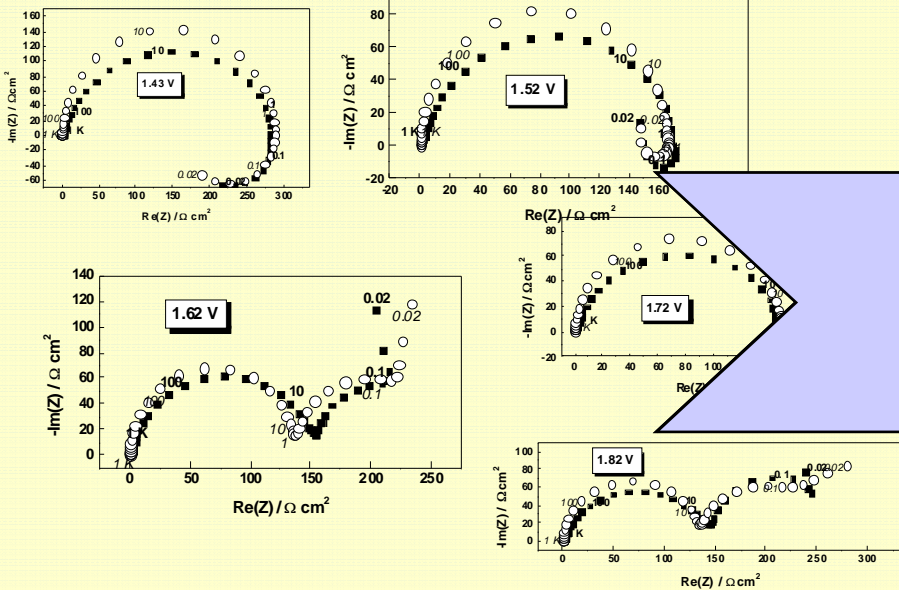
## Fe – 18% Cr



# Results – impedance (3)

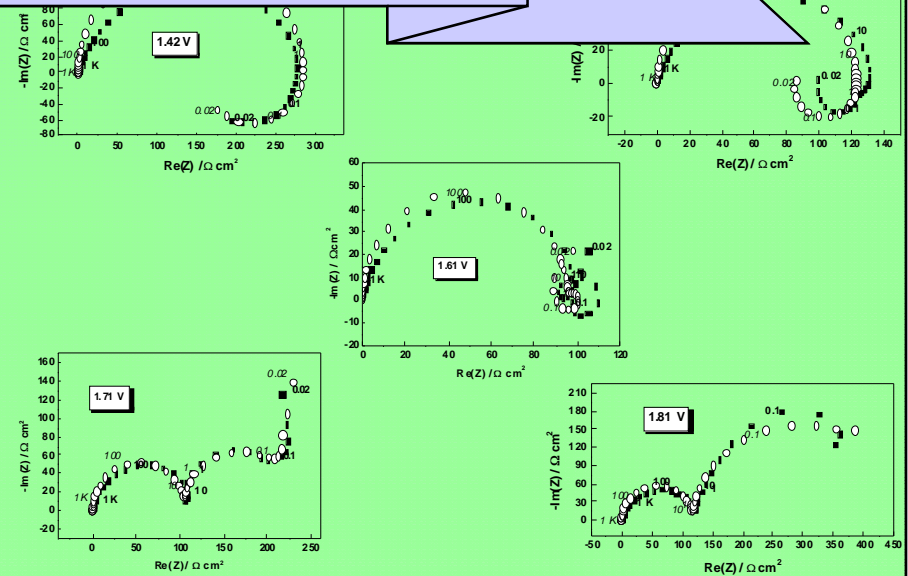


Fe – 14% Cr



Electrolyte 4

impedance at low frequencies in electrolyte 4 lower for Fe-18%Cr – etching regime

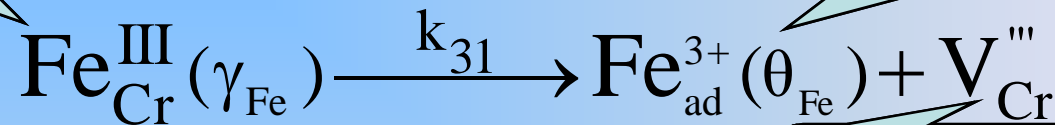


Fe – 18% Cr

# Discussion

## Reaction scheme – processes at the film / solution interface

Fe(III) in a Cr position in the surface film



adsorbed Fe(III) intermediate

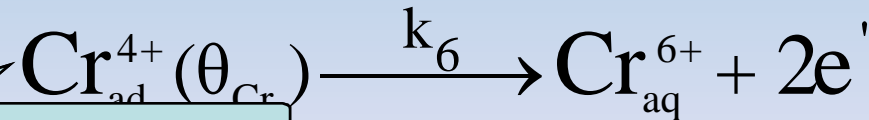


Cr cation vacancy

Cr position in the surface film



adsorbed Cr(IV) intermediate





## Discussion (2)

### Comparison with experimental data

- Material and charge balances in the steady-state and for a small amplitude AC perturbation → current-potential dependence and transfer function (Maple 6.1)
- Split the transfer function to real+imaginary parts (Maple 6.1)
- Simultaneous fit of the experimental impedances for several potentials and the current vs potential curve to the derived equations (Origin 6.0) → estimation of kinetic parameters

## Charge and material balances:

$$I = F ( 3 k_{31} \gamma_{Fe} + k_5 \gamma_{Cr} + 2 k_6 \theta_{Cr} )$$

$$\beta \frac{d \gamma_{Fe}}{d t} = k_6 \theta_{Cr} x_{Fe} - k_{31} \gamma_{Fe} + k_{32} \theta_{Fe} x_{Fe}$$

$$\beta \frac{d \gamma_{Cr}}{d t} = k_6 \theta_{Cr} x_{Cr} + k_{32} \theta_{Fe} x_{Cr} - k_5 \gamma_{Cr}$$

$$\beta \frac{d \theta_{Cr}}{d t} = k_5 \gamma_{Cr} - k_6 \theta_{Cr}$$

$$\beta \frac{d \theta_{Fe}}{d t} = k_{31} \gamma_{Fe} - k_{32} \theta_{Fe}$$

$$\frac{d \gamma_{Cr}}{d t} + \frac{d \gamma_{Fe}}{d t} + \frac{d \theta_{Cr}}{d t} + \frac{d \theta_{Fe}}{d t} = 0$$



The steady-state solution leads to an expression for the dependence of the current on potential of the form



$$\bar{I} = 3F(k_{31}\bar{\gamma}_{Fe} + k_6\bar{\theta}_{Cr})$$

$$\bar{\theta}_{Cr} = \frac{k_{31}k_{32}k_5(1 - x_{Fe})}{(k_{31} + k_{32})k_5k_6x_{Fe} + k_{31}k_{32}(k_5 + k_6)(1 - x_{Fe})}$$

$$\bar{\theta}_{Fe} = \frac{k_{31}k_5k_6x_{Fe}}{(k_{31} + k_{32})k_5k_6x_{Fe} + k_{31}k_{32}(k_5 + k_6)(1 - x_{Fe})}$$

$$\bar{\gamma}_{Cr} = \frac{k_{31}k_{32}k_6(1 - x_{Fe})}{(k_{31} + k_{32})k_5k_6x_{Fe} + k_{31}k_{32}(k_5 + k_6)(1 - x_{Fe})}$$

$$\bar{\gamma}_{Fe} = \frac{k_{32}k_5k_6x_{Fe}}{(k_{31} + k_{32})k_5k_6x_{Fe} + k_{31}k_{32}(k_5 + k_6)(1 - x_{Fe})}$$

$$\bar{\gamma}_{Cr} + \bar{\gamma}_{Fe} + \bar{\theta}_{Cr} + \bar{\theta}_{Fe} = 1$$



The solution of the system of resulting equations gives the following expression for the interfacial impedance of the system:



$$Z^{-1} = R_t^{-1} + F \frac{[3k_{31}(A_1 + jA_2) + k_5(A_3 + jA_4) + 2k_5(A_5 + jA_6)]}{A_7 + jA_8} + j\omega C_d$$

$$R_t^{-1} = F[3b_{31}k_{31}\bar{\gamma}_{Fe} + (b_5 + 2b_6)\bar{\theta}_{Cr}]$$

$$A_1 = -\omega\beta[(k_{32} + k_5 + k_6)X_1 + x_{Fe}(k_{32}X_3 + k_6X_2)]$$

$$A_2 = X_1[(k_5 + k_6)k_{32} - \omega^2\beta^2] + x_{Fe}\{k_{32}X_2k_6 + [(k_5 + k_6)k_{32} - k_5k_6]X_3\}$$

$$A_3 = \omega\beta[(k_{31} + k_{32} + k_6)X_1 + (k_{31} + k_{32} + k_6x_{Fe})X_2 + (k_{31} + k_{32}x_{Fe} + k_6)X_3]$$

$$A_4 = (X_1 + X_2 + X_3)\omega^2\beta^2 - (k_{31} + k_{32})k_6X_1 - (k_{31} + k_{32}x_{Fe})k_6X_3 - \{[(1 - x_{Fe})k_{32} + k_6x_{Fe}]k_{31} - k_{32}k_6x_{Fe}\}X_2$$

$$A_5 = \omega\beta[(X_1 + X_3)k_5 - X_2(k_{31} + k_{32})]$$

$$A_6 = (1 - x_{Fe})k_{31}k_{32}X_2 - k_5X_1(k_{31} + k_{32}) - k_5X_3(k_{31} + k_{32}x_{Fe}) - \omega^2\beta^2X_2$$

$$A_7 = \omega^3\beta^3 - \{[(1 - x_{Fe})k_{32} + k_5 + k_6]k_{31} + (k_5 + k_6)k_{32} + k_5k_6x_{Fe}\}\omega\beta$$

$$A_8 = [(1 - x_{Fe})(k_5 + k_6)k_{32} + k_5k_6x_{Fe}]k_{31} + k_{32}k_5k_6x_{Fe} - (k_{31} + k_{32} + k_5 + k_6)\omega^2\beta^2$$





## Discussion (3)

- The rate of iron dissolution - higher for Fe-14%Cr in electrolytes 1 and 3 - surface microlevelling limited by the chemical reaction of iron dissolution at the film-solution interface.
- The rate of this step the lowest in electrolyte 4 - no surface microlevelling.
- The high value of the transpassive dissolution rate of Fe – 18%Cr does not allow the formation of a stable iron-rich secondary passive film.
- Consequently, the rate of the overall process not limited by the chemical reaction at the film/solution interface alone → inferior degree of surface levelling on this alloy.





# Conclusions



- A kinetic model that comprises two parallel dissolution pathways - oxidative dissolution of Cr as chromate and isovalent dissolution of Fe(III), mediated by an adsorption/surface complexation step is proposed for the transpassive dissolution of ferritic steels
- The model involves only surface kinetic steps and reproduces successfully the steady-state and the small amplitude ac response of the studied materials
- Kinetic parameters determined by a calculation procedure that involves simultaneous fitting of the impedance spectra at several polarisation potentials and the steady state current vs. potential curve to the model equations
- An interrelationship between the surface levelling ability of different electrolytes and the velocities of the rate-determining steps of the transpassive oxidation and secondary passivation processes has been ascertained as depending on the chromium content in the alloy