

Impedance of the Catalytic EC' Processes

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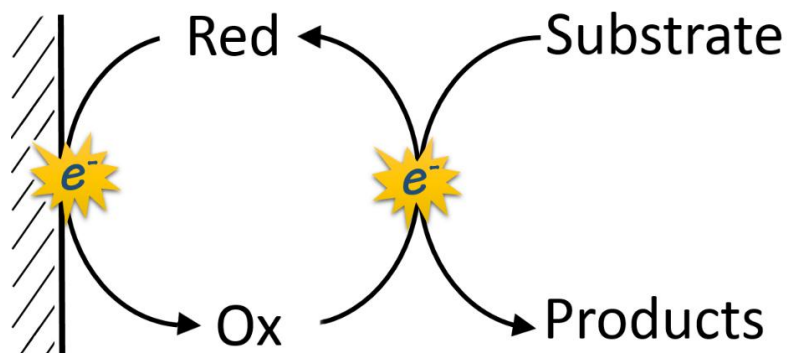


10th International Symposium
Electrochemical Impedance Analysis 2014

Outline:

- Introduction
- The model
 - Impedance, surface concentrations, spectra
 - novel impedance element
- Experimental results
 - Fenton reaction
 - Silver(I) oxidation in H_2SO_4
- Other possible applications
- Conclusions

Catalytic EC' Processes



EC' processes - why are they important?

- electrocatalysis,
- electrochemical sensors,
- catalytic hydrogen evolution,
- carbon dioxide electroreduction,
- bioanalytical applications:
 - electrochemistry of enzymes, nucleic acids and amino acids.

Previous ac treatments

Impedance:

- Solution involving unevaluated integrals¹
- Approximate solution assuming „diffusion layer theory”²

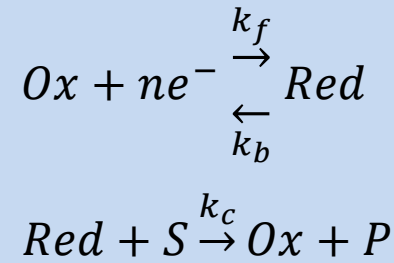
Cot(ϕ) analysis:¹

- Non-measurable directly,
- Not an additive function,
- reduced dimensionality ($\cot \phi = Z'/Z''$),
- mathematical complexity,

[1] D. Smith, *Anal. Chem.* 1963, 35, 602–609

[2] Sluyters-Rehbach et al., *J. Electroanal. Chem.* 1969, 23, 457–474

The model



$$\left\{ \begin{array}{l} \frac{\partial \Delta C_{ox}}{\partial t} = D_{ox} \frac{\partial^2 \Delta C_{ox}}{\partial x^2} + k \Delta C_{red} \\ \frac{\partial \Delta C_{red}}{\partial t} = D_{red} \frac{\partial^2 \Delta C_{red}}{\partial x^2} - k \Delta C_{red} \end{array} \right.$$

$$\Delta C_{ox} = \tilde{C}_{ox} \exp(j\omega t);$$

$$\Delta C_{red} = \tilde{C}_{red} \exp(j\omega t)$$

$$\left\{ \begin{array}{l} \frac{d^2 \tilde{C}_{ox}}{dx^2} = s_{ox}^2 \tilde{C}_{ox} + q \tilde{C}_{red} \\ \frac{d^2 \tilde{C}_{red}}{dx^2} = s_{red}^2 \tilde{C}_{red} \end{array} \right.$$

$$s_{red} = \sqrt{\frac{k + j\omega}{D_{red}}} \text{ and } s_{ox} = \sqrt{\frac{j\omega}{D_{ox}}}$$

Initial and boundary conditions

$$x = 0 \quad \frac{d\tilde{C}_{ox}}{dx} = -\frac{\tilde{i}_f}{nFAD_{ox}}; \quad \frac{d\tilde{C}_{red}}{dx} = \frac{\tilde{i}_f}{nFAD_{red}}; \quad \frac{d\tilde{C}_{ox}}{dx} + \frac{d\tilde{C}_{red}}{dx} = 0$$

$$x \rightarrow \infty \quad \tilde{C}_{ox} \rightarrow 0 \text{ and } \tilde{C}_{red} \rightarrow 0$$

Faradaic impedance

$$Z_f = \frac{\tilde{E}}{\tilde{i}_f} = \frac{RT}{n^2 F^2 A} \frac{\left(1 + \frac{k_f}{D_{ox} s_{ox}} + \frac{k_b}{D_{red} s_{red}} - \frac{k k_f}{\sqrt{j\omega} \sqrt{k + j\omega} (\sqrt{D_{ox}} \sqrt{k + j\omega} + \sqrt{D_{red}} \sqrt{j\omega})} \right)}{\beta k_b C_{red}(0) + \alpha k_f C_{ox}(0)}$$

where

$$s_{red} = \sqrt{\frac{k + j\omega}{D_{red}}} \text{ and } s_{ox} = \sqrt{\frac{j\omega}{D_{ox}}}$$

Surface concentrations

$$\left\{ \begin{array}{l} \frac{\partial C_{\text{ox}}}{\partial t} = D_{\text{ox}} \frac{\partial^2 C_{\text{ox}}}{\partial x^2} - k C_{\text{ox}} \\ \frac{\partial C_{\text{red}}}{\partial t} = D_{\text{red}} \frac{\partial^2 C_{\text{red}}}{\partial x^2} + k C_{\text{ox}} \end{array} \right. \quad \left\{ \begin{array}{l} \frac{d^2 C_{\text{ox}}}{dx^2} = \frac{k}{D_{\text{ox}}} C_{\text{ox}} \\ \frac{d^2 C_{\text{red}}}{dx^2} = -\frac{k}{D_{\text{red}}} C_{\text{ox}} \end{array} \right.$$

boundary conditions:

$$x = 0 \quad \frac{d\tilde{C}_{\text{ox}}}{dx} = k_f C_{\text{ox}}(0) - k_b C_{\text{red}}(0)$$

$$x \rightarrow \infty \quad C_{\text{ox}} \rightarrow 0 \text{ and } C_{\text{red}} \rightarrow C_{\text{red}}^*$$

Solution:

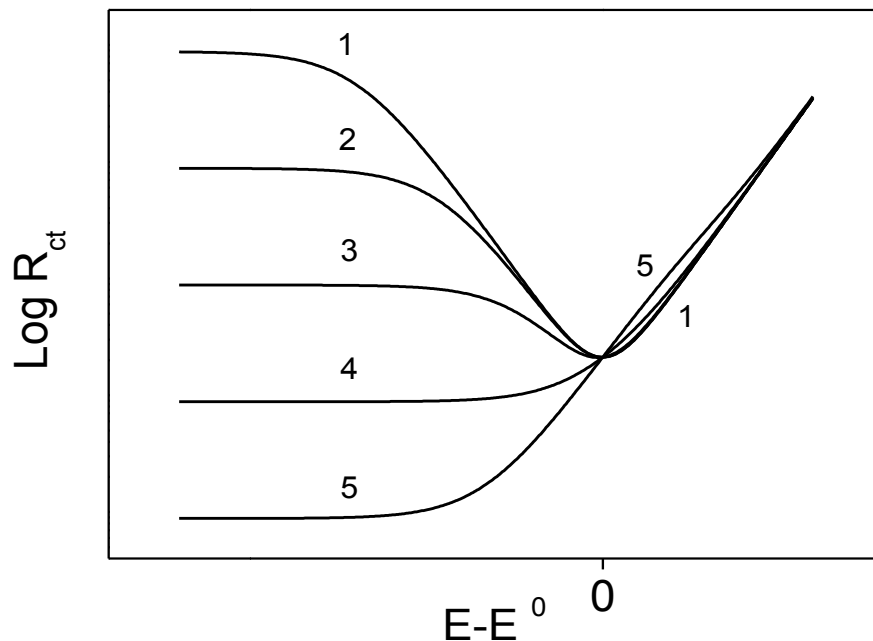
$$C_{\text{red}}(x) = C_{\text{red}}^* \left(1 - \frac{D_{\text{ox}} k_b}{\sqrt{D_{\text{ox}}} D_{\text{red}} \sqrt{k} + D_{\text{ox}} k_b + D_{\text{red}} k_f} e^{-\frac{\sqrt{k}}{\sqrt{D_{\text{ox}}}} x} \right)$$

$$C_{\text{ox}}(x) = C_{\text{red}}^* \frac{D_{\text{red}} k_b}{D_{\text{ox}} D_{\text{red}} \sqrt{k} + D_{\text{ox}} k_b + D_{\text{red}} k_f} e^{-\frac{\sqrt{k}}{\sqrt{D_{\text{ox}}}} x}$$

R_{ct} – potential dependence

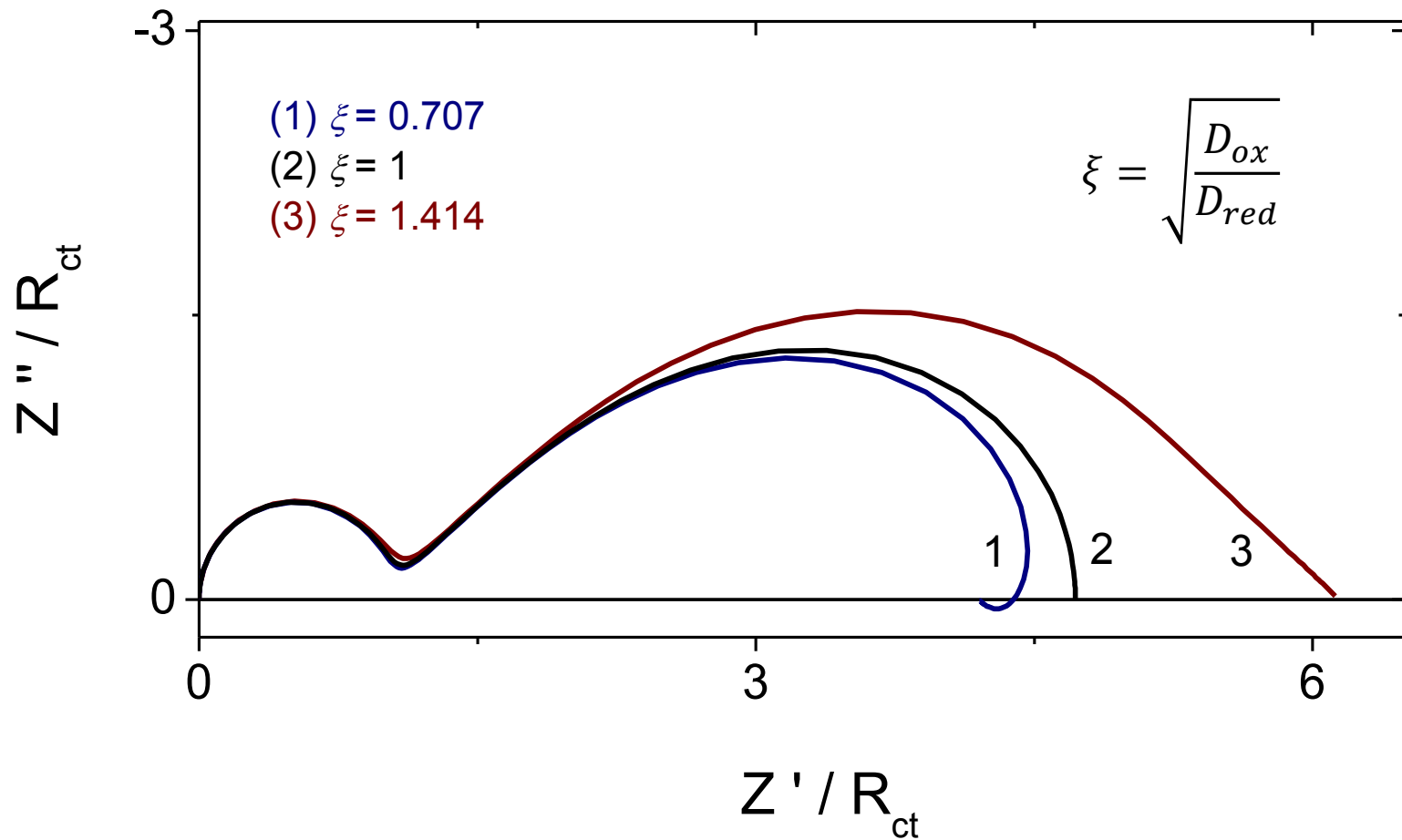
$$R_{ct} = \frac{RT}{n^2 F^2 A C_{ox}^* D_{ox} k_f} \frac{D_{red} k_f + D_{ox} (\sqrt{D_{red} k} + k_b)}{\alpha \sqrt{D_{red} k} + (\alpha + \beta) k_b}$$

$$R_{ct}(E \ll E^{0'}) = \frac{RT \sqrt{D_{red}}}{n^2 F^2 A \alpha C_{ox}^* D_{ox} \sqrt{k}}$$

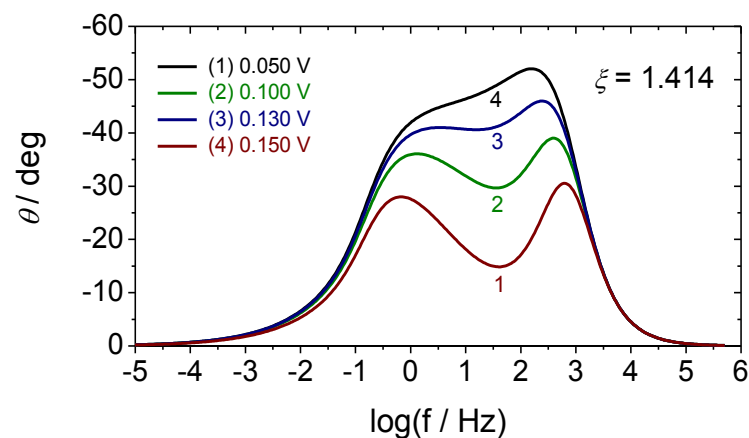
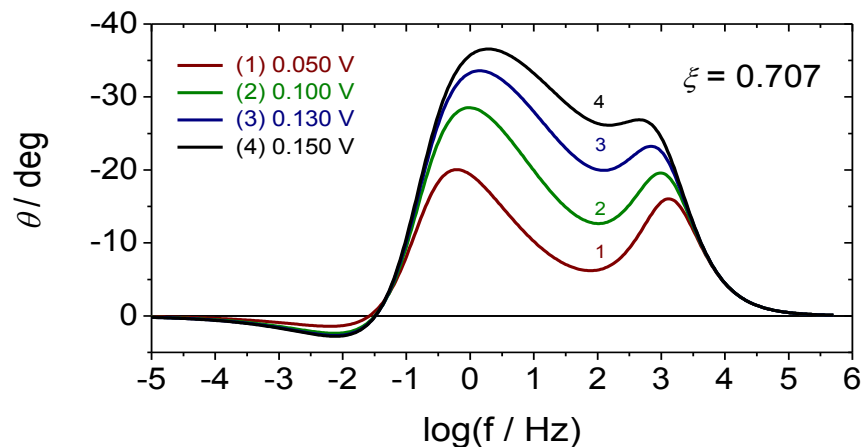
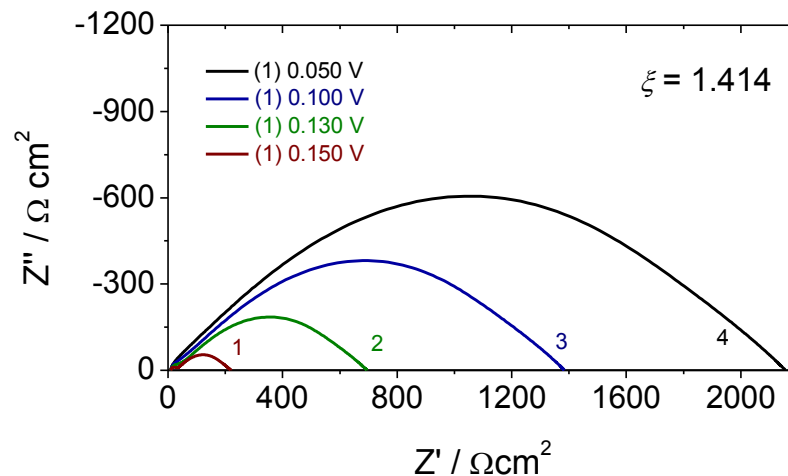
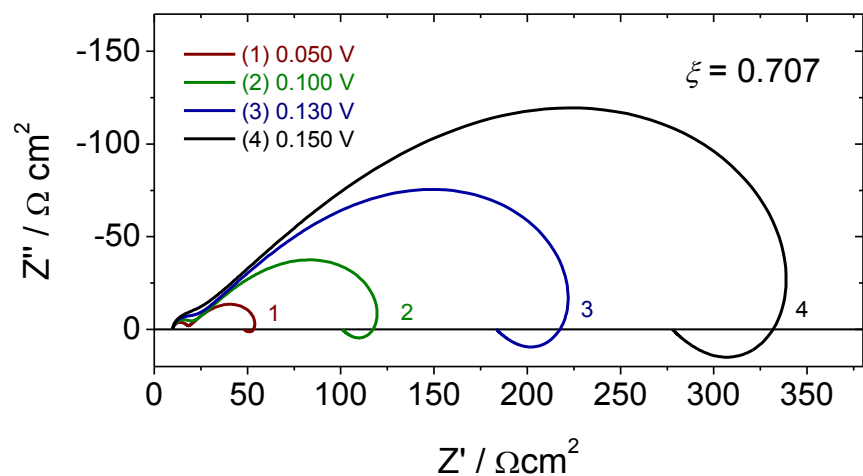


k/k_0 [cm^{-1}]: (1) 10^0 , (2) 10^2 , (3) 10^4 , (4) 10^6 , (5) 10^8 .

The influence of diffusion coefficients (theoretical spectra for the EC' process)

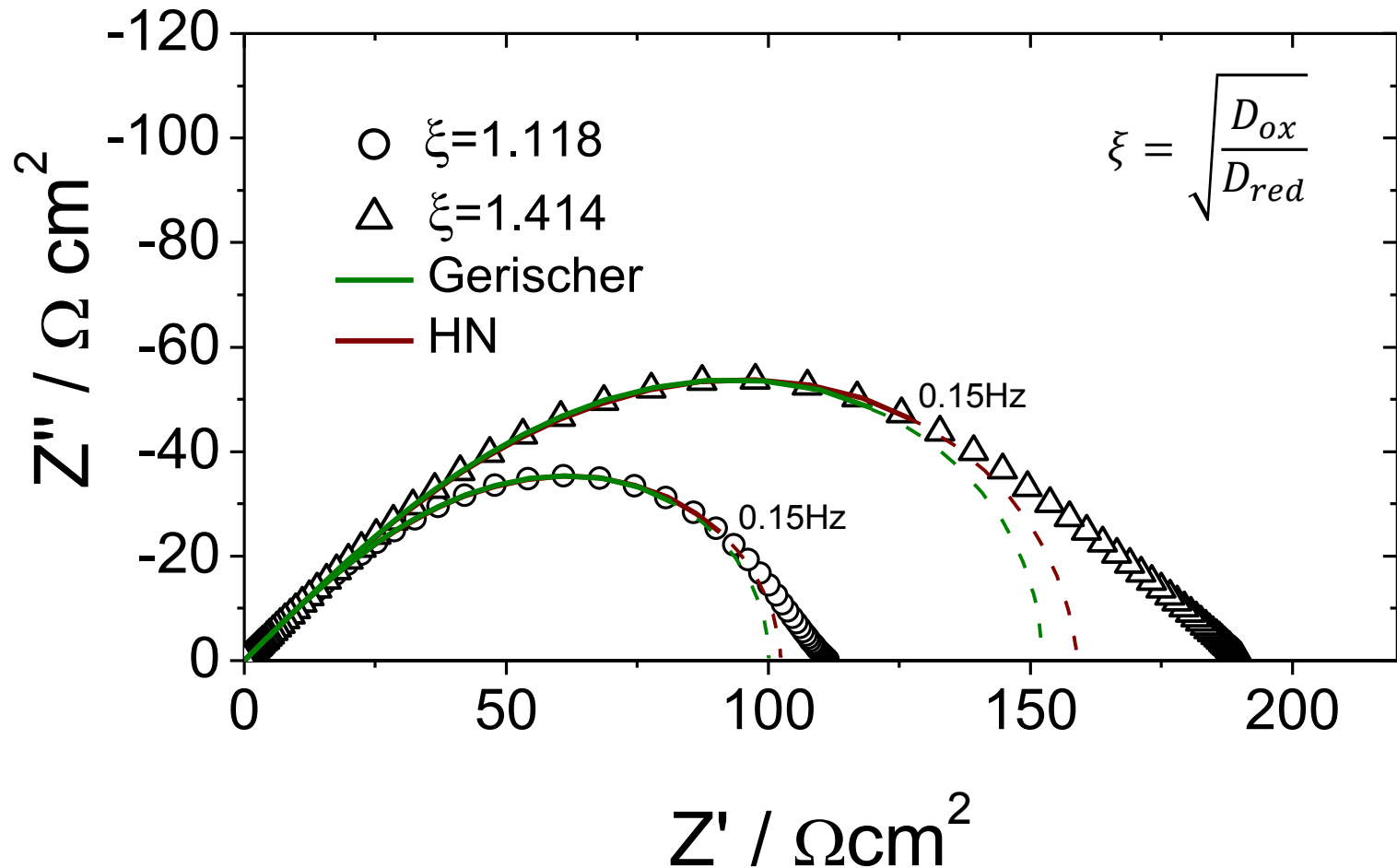


The influence of diffusion coefficients (theoretical spectra for the EC' process)



Spectra fitting

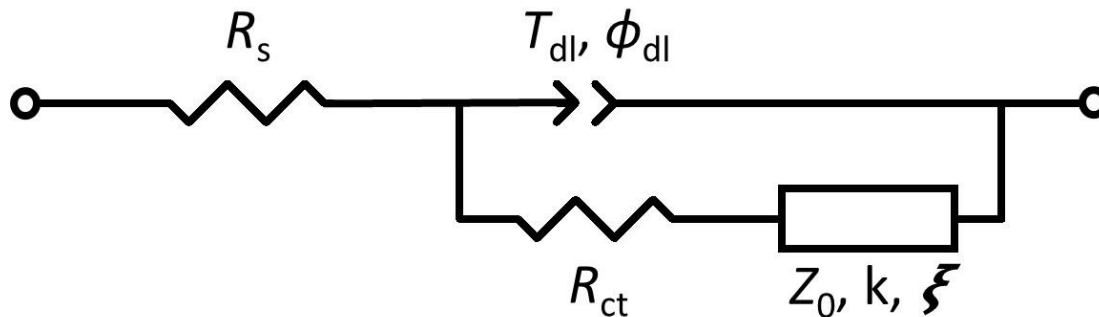
(theoretical spectra for the EC' process)



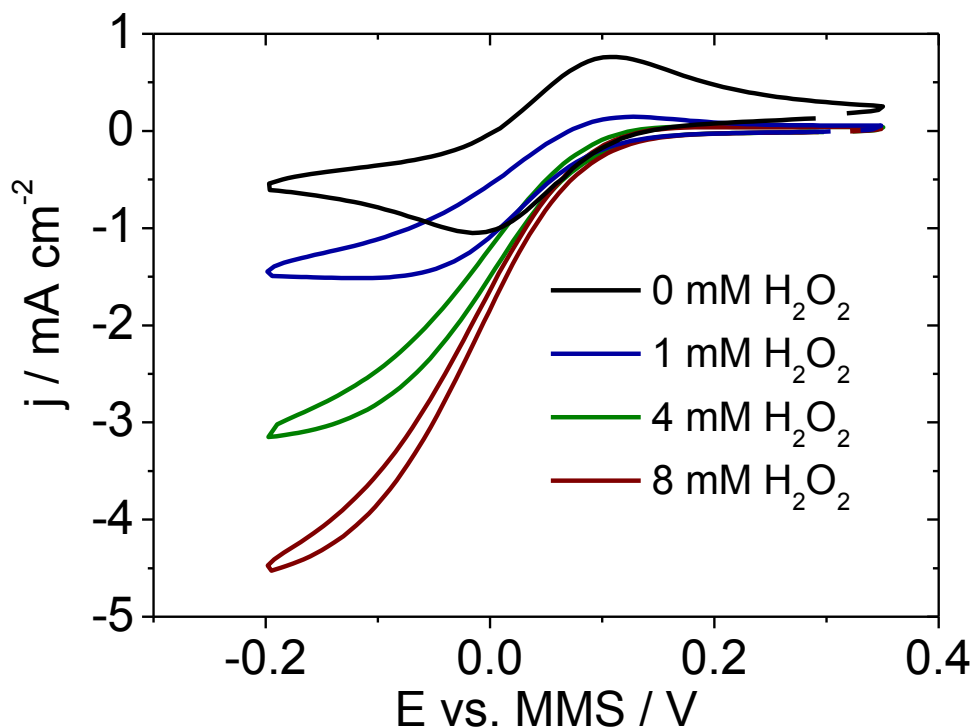
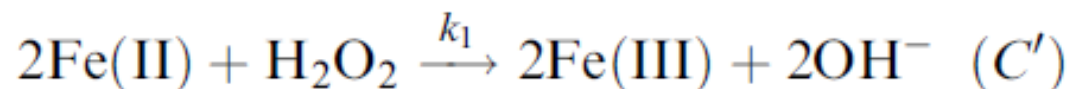
Faradaic impedance

$$\hat{Z}_f = R_{ct} + \frac{1}{\sqrt{j\omega + k}} \hat{Z}_\xi \quad \hat{Z}_\xi = Z_1 \frac{\xi + a}{1 + \xi a} \quad a = \frac{\sqrt{j\omega}}{\sqrt{j\omega + k}}$$

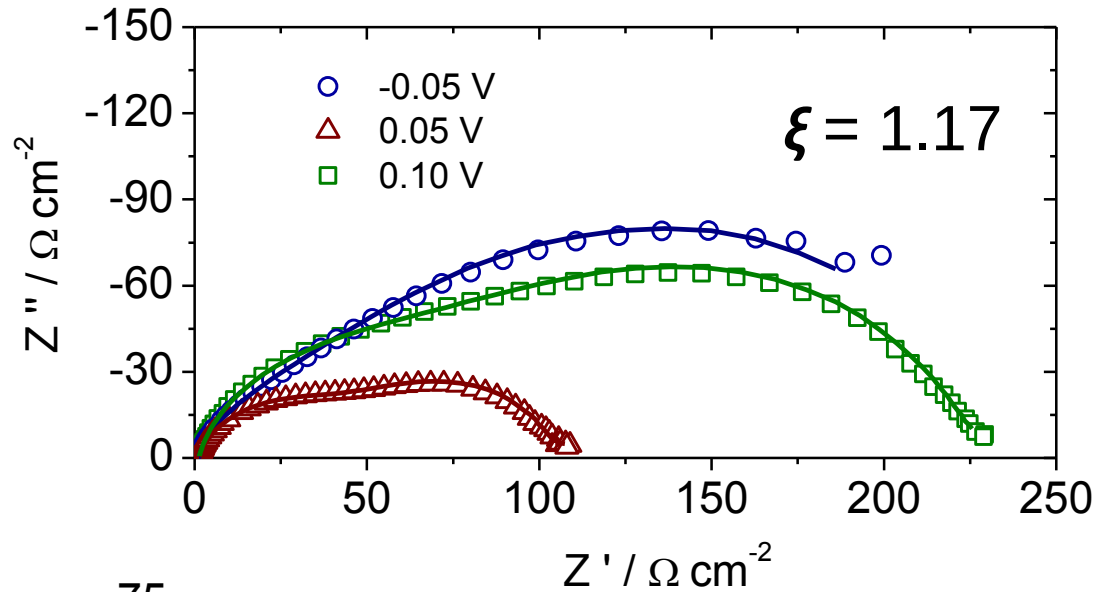
$$Z_1 = \frac{R_{ct} k_f}{\sqrt{D_{red}}}; \quad \xi = \sqrt{\frac{D_{ox}}{D_{red}}}$$



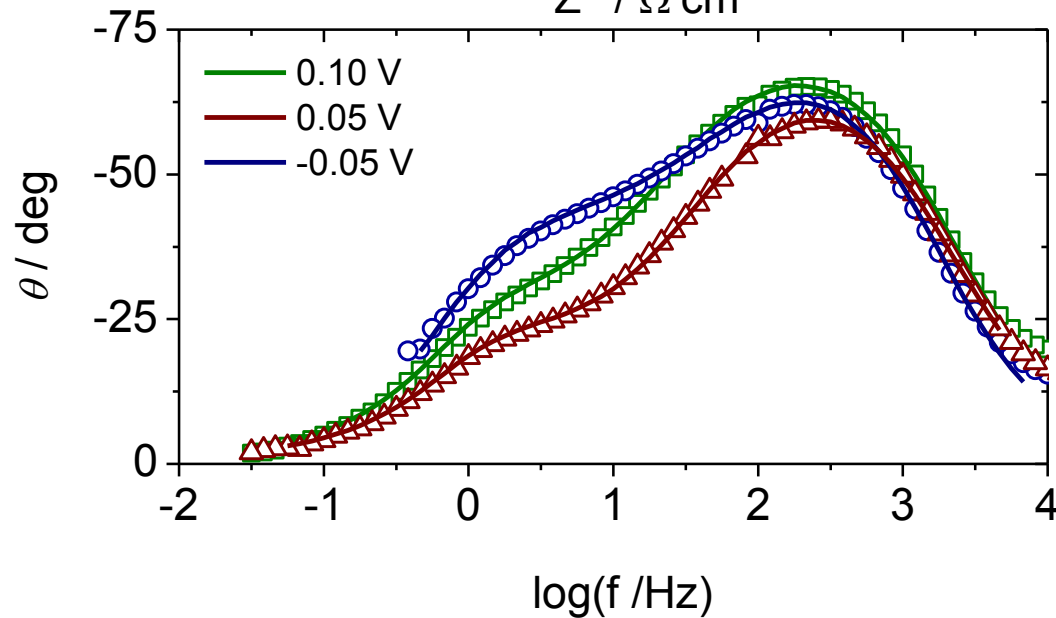
Fenton reaction. Cyclic voltammetry



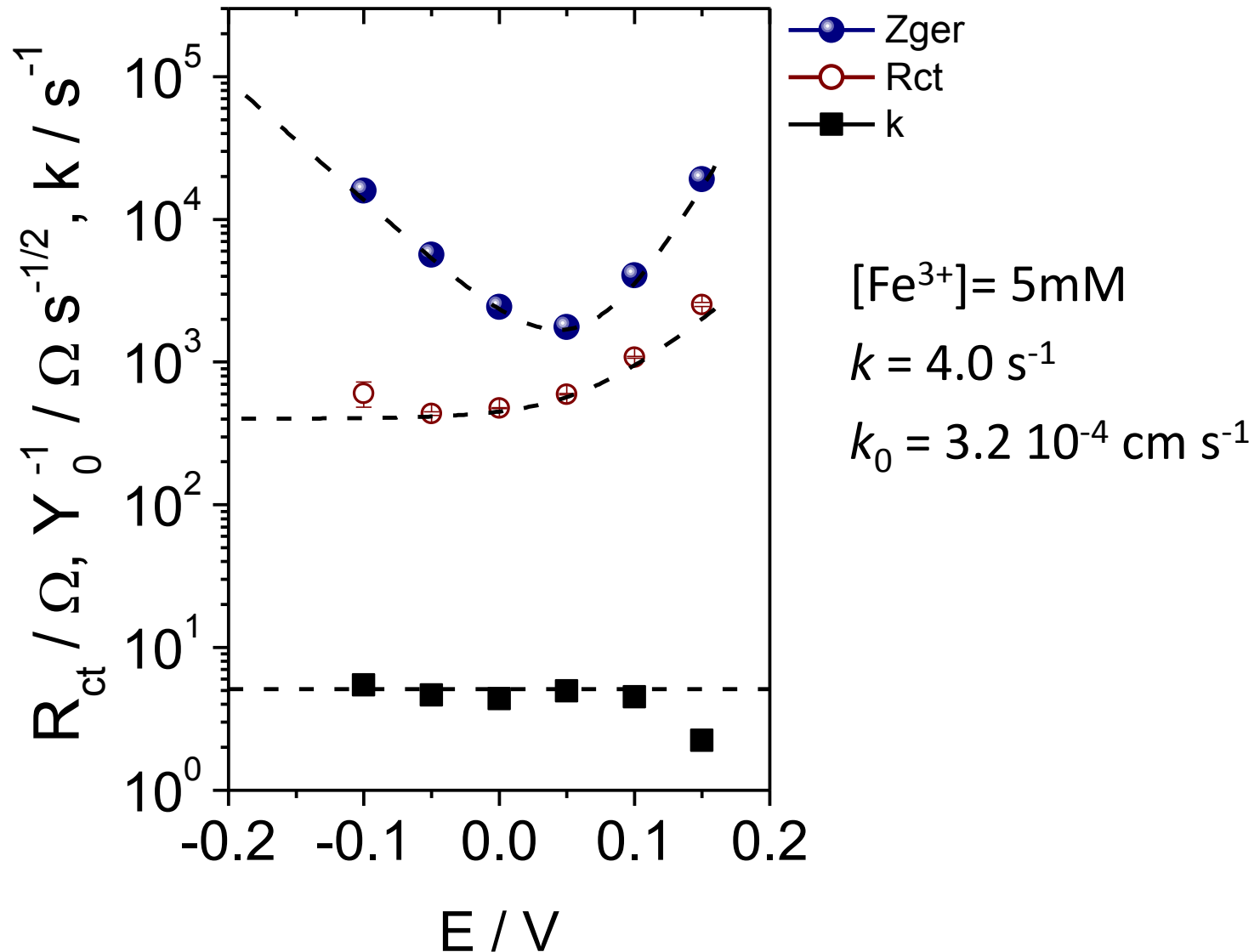
Impedance of Fenton reaction



$$\xi = \sqrt{\frac{D_{\text{red}}}{D_{\text{ox}}}}$$

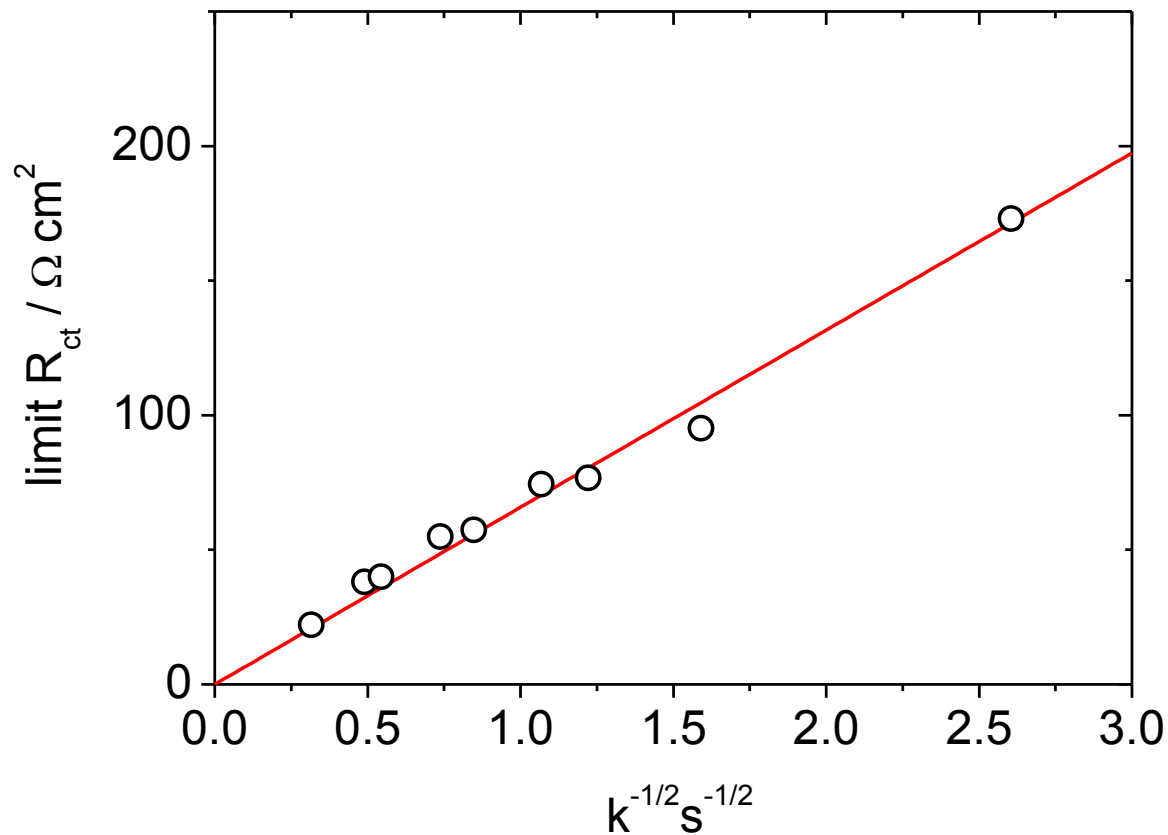


Fenton reaction - Impedance parameters

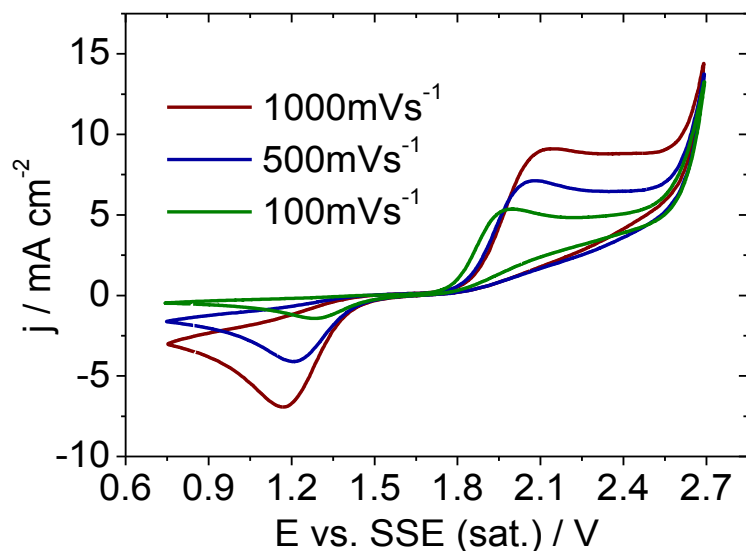


R_{ct} – cathodic limit at $E \ll E^{0'}$

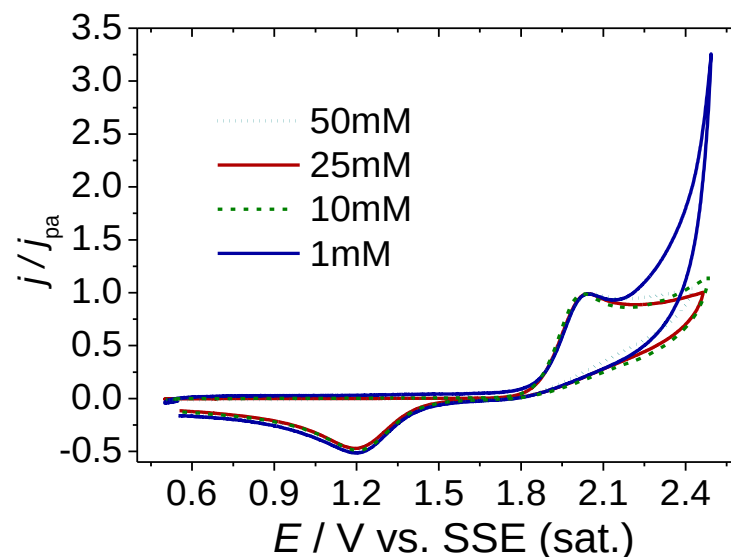
$$R_{ct}(E \ll E^{0'}) = \frac{RT\sqrt{D_{red}}}{n^2F^2A\alpha C_{ox}^*D_{ox}\sqrt{k}}$$



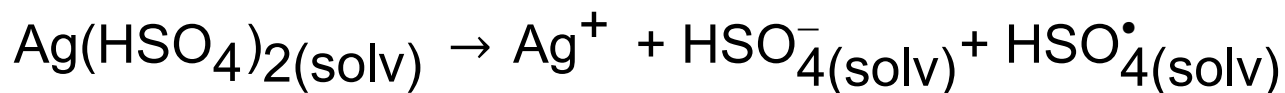
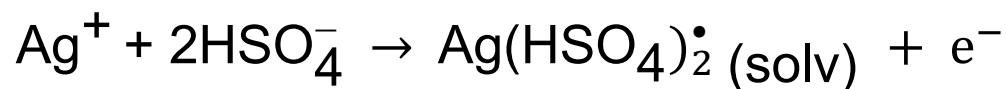
Silver(I) oxidation – cyclic voltammetry



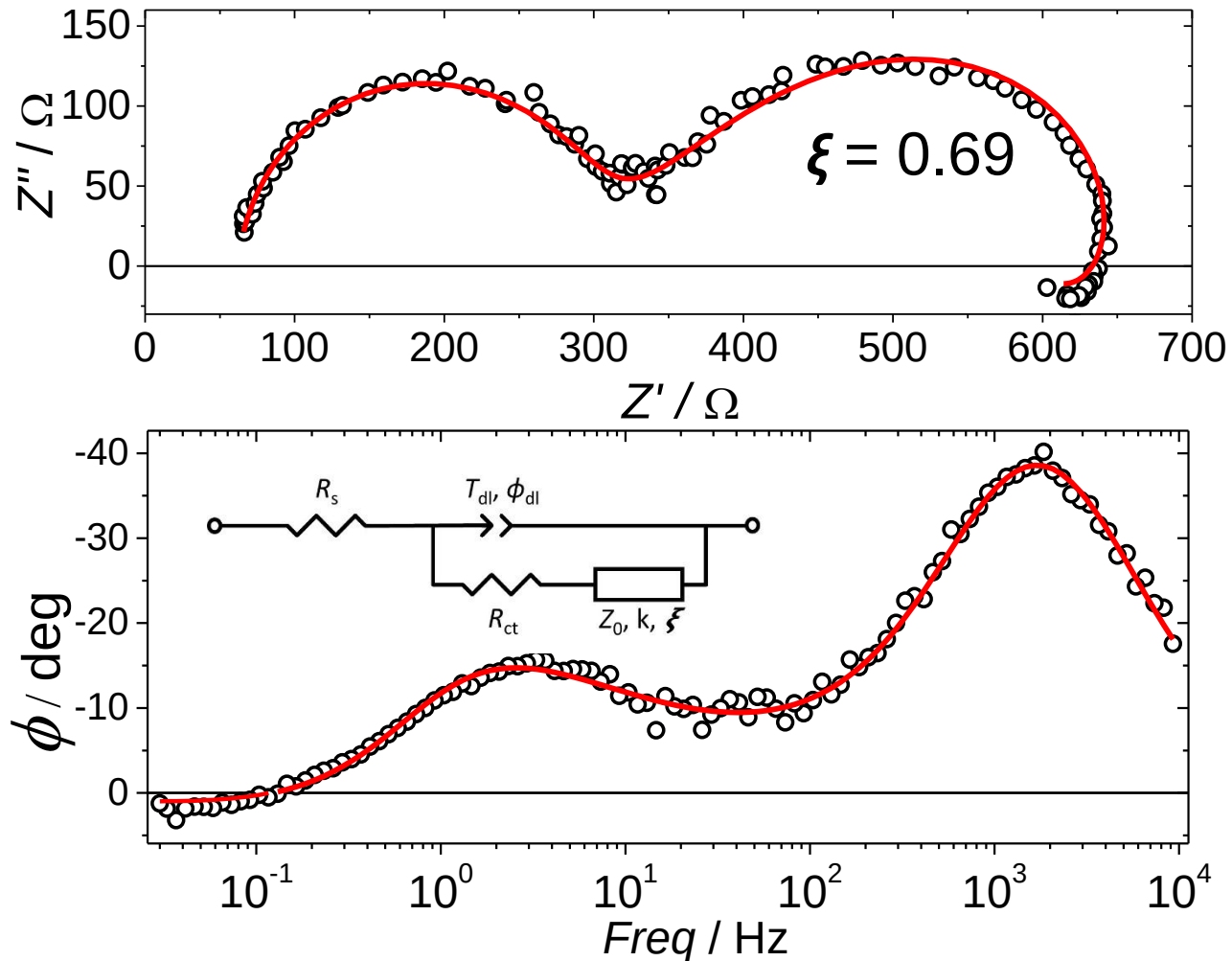
50mM Ag(I)



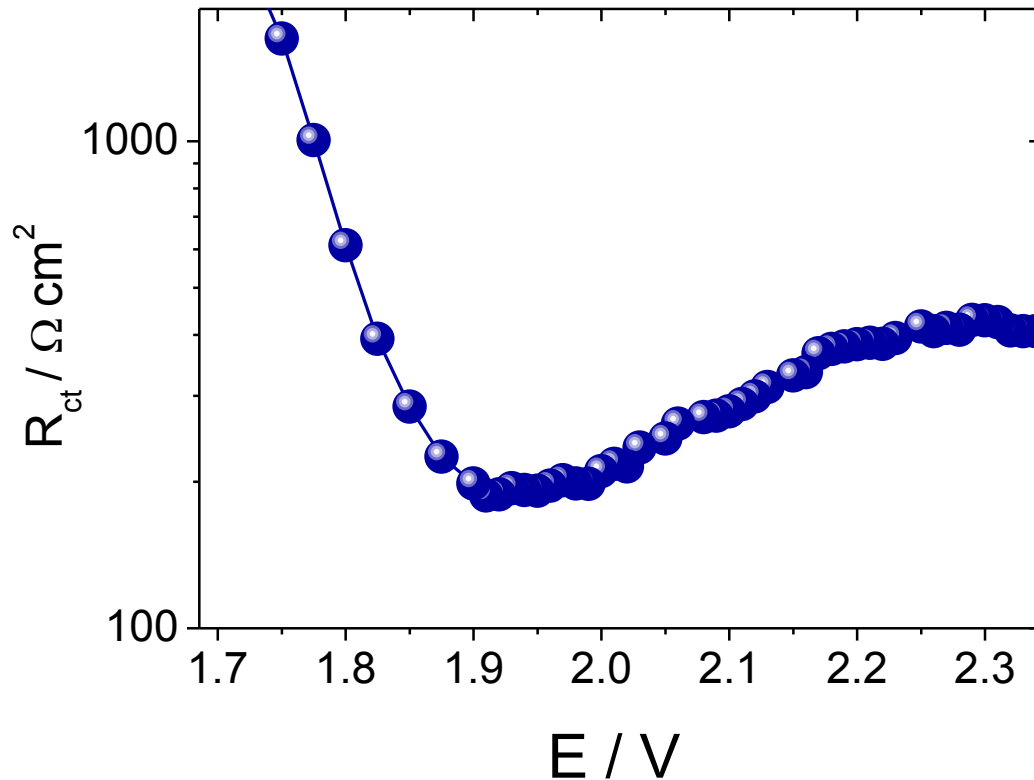
$v=500 \text{ mV} \cdot \text{s}^{-1}$



Fitting of the experimental spectra for Ag(I) oxidation



Potential dependence of R_{ct} Ag(I) oxidation



$$C_{\text{Ag}^+} = 5\text{mM}$$

$$k = 0,1 \text{ s}^{-1}$$

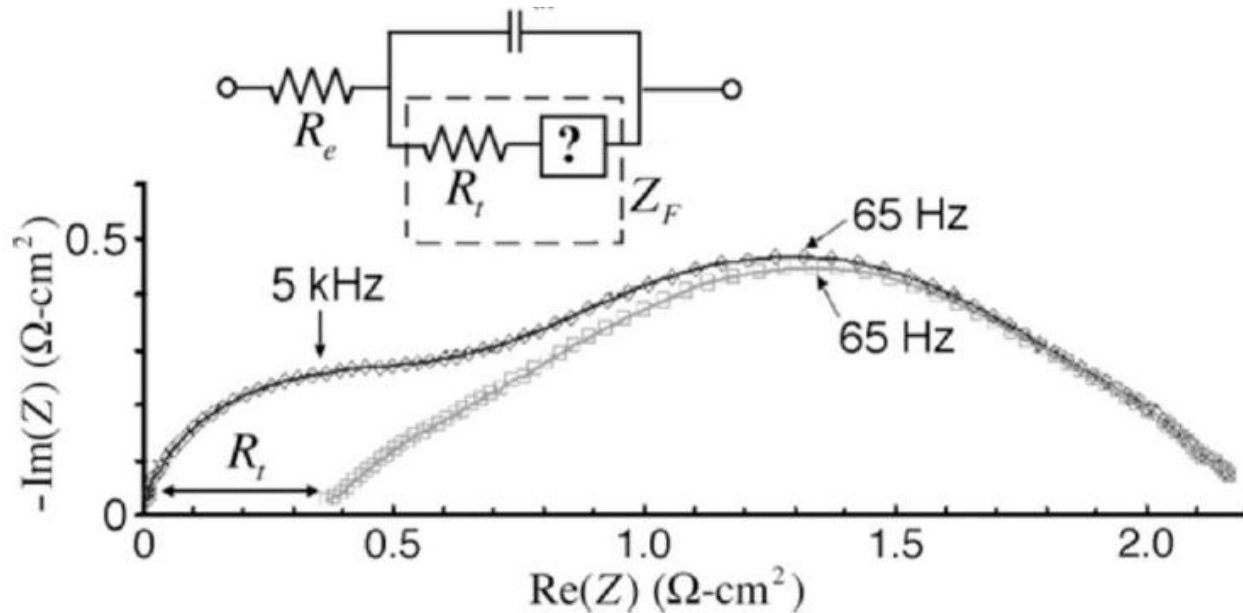
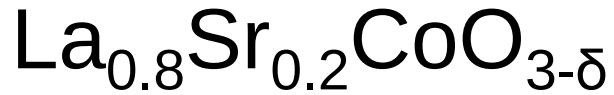
$$k_0 = 10^{-6} \text{ cm s}^{-1}$$

$$D_{\text{ox}} = 2,5 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$$

$$D_{\text{red}} = 4.2 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1},$$

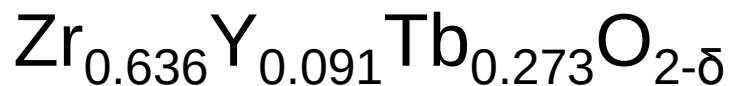
$$\alpha = 0.4 \quad \beta = 0.6$$

Other possible applications. Solid state ionics



Lu, X; Kreller, C; Adler, S., J. Electrochem. Soc., 2009, 156, B513-B525

Other possible applications. Solid state ionics



Impedance Studies on Chromite-Titanate Porous Electrodes under Reducing Conditions.²

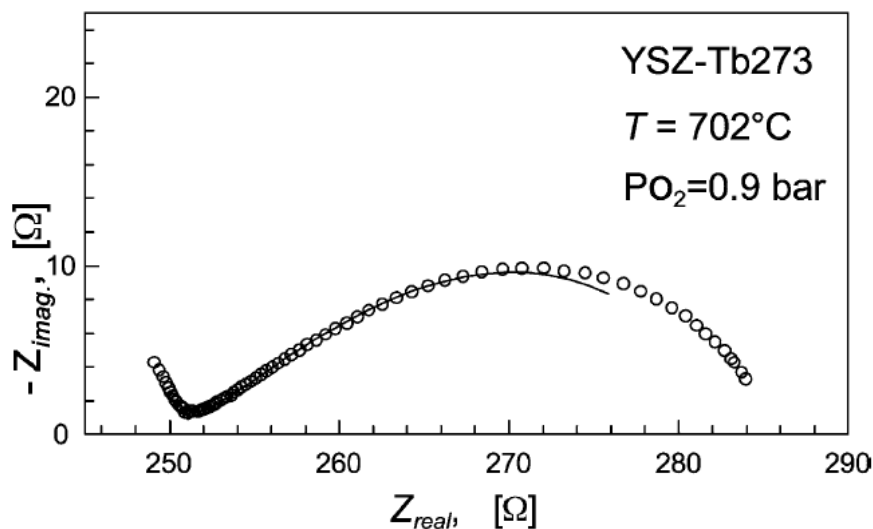


Fig. 4. Impedance diagrams for the YSZ–Tb273 sample with blocking gold electrodes. The continuous line presents the CNLS model.

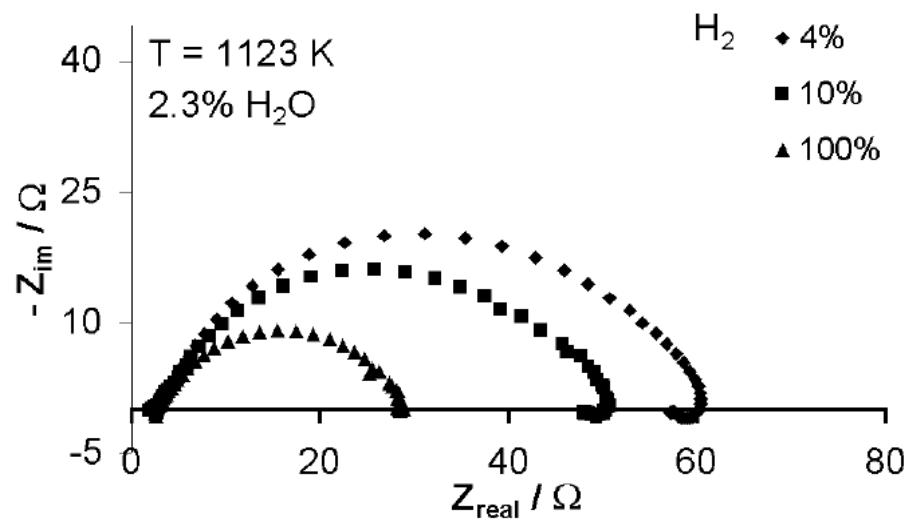


Fig. 5 Hydrogen partial pressure dependence of electrode impedance for a 100 μm thick LSCT 7382 anode.

1. Boukamp, B.A.; Bouwmeester, H.J.M., Solid State Ionics, **2003**, 157, 29-33
2. Gonzalez-Cuenca, M.; Zipprich, W.; Boukamp, B. A.; Pudmich, G.; Tietz, F., Fuel Cells 2001, 1, 256-264.

Conclusions

Analytical solution for EC' processes was obtained in the rigorous treatment together with the potential-dependence of all impedance parameters.

The analytical expression for this limiting R_{ct} value allows for determination of many important kinetic and thermodynamic parameters of the catalytic systems.

Systems with unequal diffusivities of the redox mediator have a strong effect on the impedance characteristics of the catalytic EC' systems. This behavior is related to the novel impedance element derived in this study.

Impedance features characteristic to the novel element have been frequently reported in the experimental studies in solid state Ionics.



Acknowledgement

N N204 275638 grant

Polish Ministry of Science and Higher Education

Homogeneous reaction rate constants

