

## Electrochemical properties of Ag(II) in concentrated sulfuric acid solutions.

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Novel functional materials are of significant relevance to the development of numerous industrial technologies such as electronics and renewable energy sources. Compounds of divalent silver are particularly interesting due to their unusual physicochemical properties. Recently prepared sulfate of divalent silver [1] has a narrow electronic band gap with a pronounced free radical character of sulphate anions. It's a rare example of a one-dimensional antiferromagnetism, persisting until the thermal decomposition in 110°C.

Electrochemically generated divalent silver can also be used as an extinction agent for greenhouse gases in flow reactor or for oxidation of organic chemical pollutions. Due to high standard potential of the Ag(I)/Ag(II) redox couple divalent silver compounds cannot be formed in solutions containing unbounded water. Moreover, solvent, electrolyte, and electrode material itself has to be highly resistant to oxidation. To date, electrochemical oxidation of Ag(I) was studied mostly in nitric and perchloric acids of moderate concentrations. It has been shown that under these conditions the clathrate  $\text{Ag}_7\text{O}_8^+$  species are formed [2]. From Pourbaix diagram it follows that Ag(II) can be only produced in solutions more acidic than  $\text{pH} = -2$ . Here we report electrochemical studies of silver(I) oxidation in concentrated sulfuric acid and oleums at FTO (Fluorine-doped Tin Oxide) electrodes. Electrochemical processes taking place at the electrode/solution interface have been investigated with classical transient methods and Electrochemical Impedance Spectroscopy (EIS). Results indicate that the electrooxidation proceeds according to EC mechanism, that is the electron transfer is followed by a homogenous chemical reaction. Exemplary impedance spectrum and the equivalent circuit used for data analysis is shown in Fig. 1. Shape of this spectrum is characteristic for EC processes. By fitting impedance spectra selected kinetic and thermodynamic parameters were determined. The kinetics of the homogenous chemical step was included in the model as Gerisher element (GE). Resistance of the charge transfer for silver(I) oxidation is presented in Fig. 2. Obtained curve is characteristic for quasi-reversible electrode process. In order to identify the chemical nature of the final product we performed batch electrolysis. The obtained black powder was analyzed by using XRD, ESR, SQUID. Results indicate that we synthesized new compound of divalent silver or an unknown phase of  $\text{AgSO}_4$ .

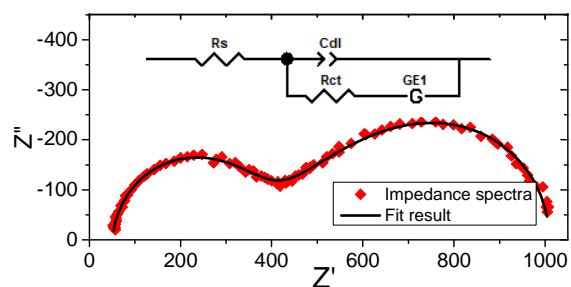


Fig. 1. Impedance spectrum of Ag(I) oxidation in 18 M(95%)  $\text{H}_2\text{SO}_4$ , 20mM Ag(I) at FTO electrode. Black continuous line (—) represent the fit result of experimental points (♦) by using equivalent circuit shown in inset.

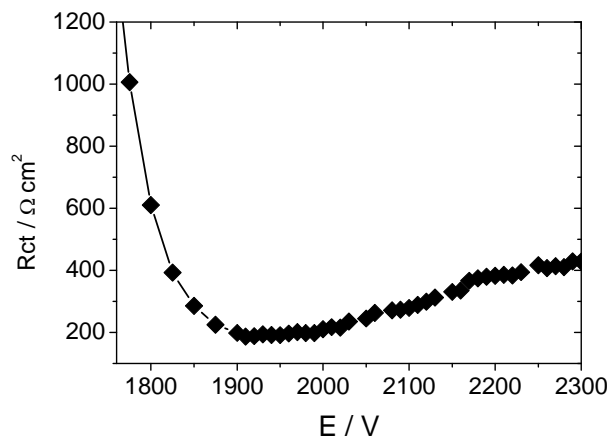


Fig. 2. Resistance of charge transfer of Ag(I) oxidation in 18 M(95%)  $\text{H}_2\text{SO}_4$ , 20mM Ag(I) at FTO electrode in function of applied potential.

### References:

- [1] Malinowski, P. J., Derzsi, M., Mazej, Z., Jagličić, Z., Gawel, B., Łasocha, W., & Grochala, W. (2010). *Angewandte Chemie (International ed. in English)*, 49(9), 1683–6. doi:10.1002/anie.200906863
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