



# Electroreduction of Cr(III) Ions in Methanesulphonate Solution on Pb Electrode

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Received 8 March 2011; Accepted 30 April 2011

**Abstract:** The electrochemical reduction of Cr(III) methanesulphonate complexes were investigated on the lead electrode. The Cr(III) electroreduction process proved to be irreversible. The standard rate constants as well as the standard electrode potentials of Cr(III) ions in methanesulphonic acid (MSA) solution are less than those corresponding to the perchlorate electrolytes.

**Keywords:** Electroreduction, Chromium(III) ions, Methanesulphonic acid.

## Introduction

Kinetics and mechanism of Cr(III) incomplete electroreduction have been investigated both on mercury and different solid electrodes<sup>1-14</sup>. Such studies have not only theoretical value but also concern an important problem of trivalent chromium electroplating. The electrochemical reaction is known to be a first stage in the stepwise electrochemical reaction of chromium deposition from Cr(III) baths<sup>15</sup>, which have being investigated in terms of environmental considerations. Evidently, kinetics of reaction (Eqn. 1) affects the rate of the overall electrochemical process of chromium electrodeposition.



Recently, environment-friendly Cr(III) baths containing methanesulphonic acid (MSA) were proposed<sup>16,17</sup>. The electroplating baths containing MSA are known to have many advantages<sup>18</sup>. However, kinetics of Cr(III) electroreduction in such electrolytes is still unexplored.

## Experimental

All solutions were prepared using doubly distilled water and reagent grade chemicals. Voltammograms were recorded by means of potentiostat/galvanostat reference 3000 (Gamry).

All electrochemical experiments were performed at  $298 \pm 0.1$  K in a glass three-electrode cell deaerated by blowing with electrolytic hydrogen. The cathodic and anodic compartments were separated with a porous glass diaphragm.

The working electrode was an end face of a platinum cylinder embedded into glass on which a Pb-coating was deposited prior each experiment. The Pb bath contained ( $\text{g L}^{-1}$ ):  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$  134,  $\text{CH}_3\text{SO}_3\text{H}$  (free) 100, organic additive<sup>1,2</sup>. Lead coating with a thickness of  $10 \mu\text{m}$  was deposited at  $2 \text{ A dm}^{-2}$  and 298 K.

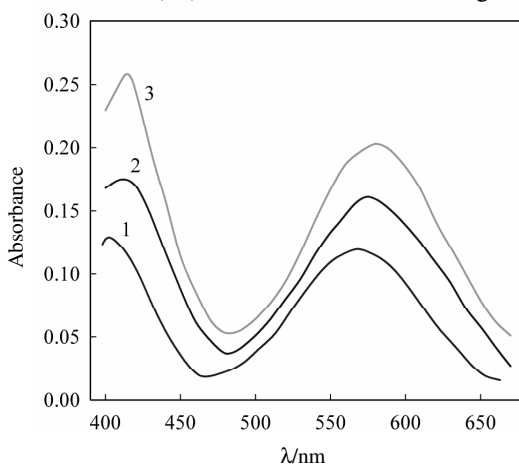
The counter electrode was made of platinum wire. All potentials were measured with respect to the saturated Ag/AgCl-electrode and recalculated to a standard hydrogen electrode.

A UV/Vis spectrophotometer SF-46 was used to obtain the visible absorption spectra. Absorption layer thickness was 1 cm. The equilibrium geometric structures of the Cr(III)-complexes were optimized using quantum-mechanical calculation (HyperChem, Ver. 8.0; semi-empirical Method PM3)<sup>19</sup>. A specially selected organic additive for MSA containing Pb bath is earlier described in the literature<sup>20</sup>.

## Results and Discussion

### *Absorption spectrum characterization and quantum-mechanical simulation*

The absorption spectra of some Cr(III)-solutions are shown in Figure 1.



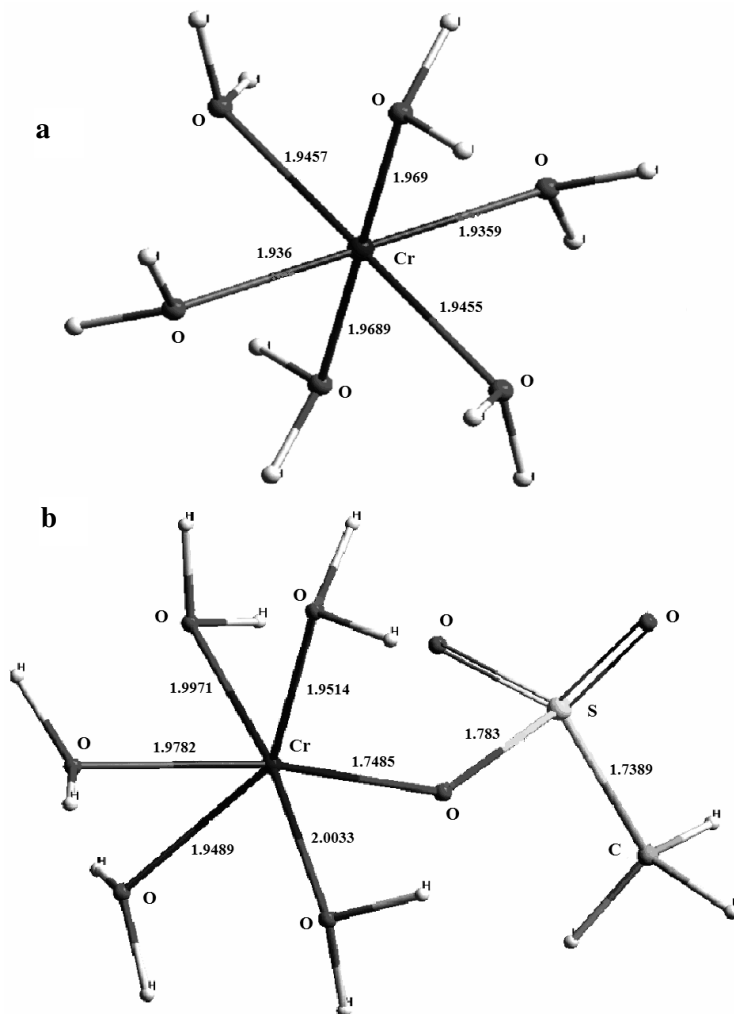
**Figure 1.** Visible spectra in aqueous Cr(III) solutions (0.01 M Cr(III)), (1) chromium(III) perchlorate (*violet form*); (2) chromium(III) methanesulphonate (*fresh prepared violet form*); (3) chromium(III) methanesulphonate (*green form obtained after keeping solution during two weeks at ambient temperature*)

Cr(III) ions are known to exist exclusively in the aqua-form  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  in perchlorate solutions. Two peaks at  $\lambda_{\text{max},1} = 410 \text{ nm}$  and  $\lambda_{\text{max},2} = 575 \text{ nm}$  appear in such a medium. Replacement reactions of  $\text{H}_2\text{O}$ -molecules in the inner coordination sphere of aqua-complex  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  is well-known to occur only with considerable kinetics deceleration<sup>21</sup>.

Freshly made methanesulphonate solutions of Cr(III) are colored violet just like perchlorate one (at least, during one hour after their preparation). However, the absorption peaks are slightly shifted to the longer wavelengths ( $\Delta\lambda_{\text{max},1} = \Delta\lambda_{\text{max},2} \approx 2 \text{ nm}$ ) and the absorption

intensity increases noticeably (Figure 1, curve 2). This points out that the MSA-complexes of Cr(III) are formed. Apparently, one or several H<sub>2</sub>O molecules in the inner sphere of aqua-complex are replaced with methanesulphonate-anion(s).

Figure 2a shows the calculated equilibrium octahedron geometrical structure of [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> complex where Cr<sup>3+</sup> ions locates at the center. The calculated equilibrium geometry of [Cr(H<sub>2</sub>O)<sub>5</sub>CH<sub>3</sub>SO<sub>3</sub>]<sup>2+</sup> is presented in Figure 2b. This complex ion exhibits irregular-octahedron structure.



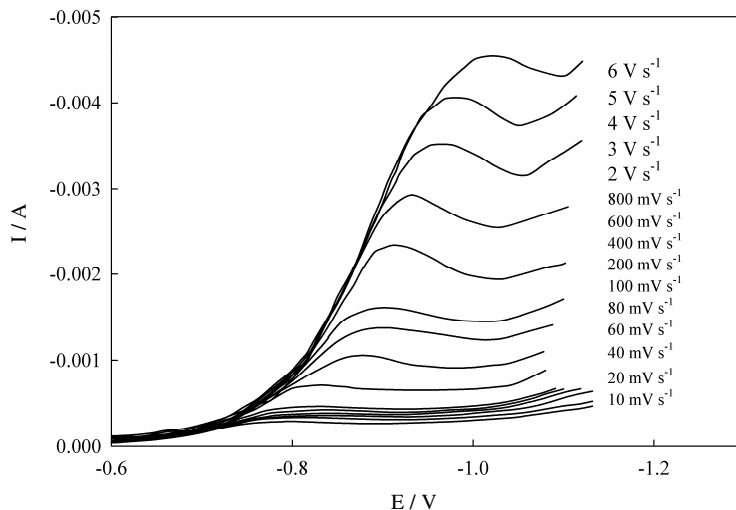
**Figure 2.** Equilibrium geometric structure of Cr(III) complexes (a) [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>; (b) [Cr(H<sub>2</sub>O)<sub>5</sub>CH<sub>3</sub>SO<sub>3</sub>]<sup>2+</sup>

As is generally known, violet and green forms of Cr(III) ions exist in aqueous sulfate solutions<sup>21-23</sup>. A violet modification of Cr(III) sulfate salt (aqua-complexes and mononuclear complexes) is transformed progressively into a green form which consists of polymerized polynuclear complexes containing sulfato-, ol-, oxo-bridges<sup>21,24,25</sup>. We have confirmed that the same phenomenon occurs in the case of methanesulphonate solutions.

Indeed, as stated above, a fresh chromium(III) methanesulphonate solution is violet. When keeping this solution during two weeks at ambient temperature, it gradually becomes green. Simultaneously, its visible spectrum changes (Figure 1, curve 3). Both absorption peaks shift substantially to the greater wavelengths and the absorbance increases<sup>1</sup>. All these phenomena may indicate that polymerized complexes are generated by formation of ol- and oxo-bridges.

### Voltammetry study

Since lead electrode was obtained by electroplating, the real surface area of the electrode differs from its visible value. In order to estimate the real surface area of the electrodeposited electrodes, we used the method based on measuring differential capacitance of a double electrical layer of the electrode<sup>26</sup>. The obtained value of electrode roughness factor proved to be equal to 1.26. All rate constants were calculated taking into account the roughness factor of the electrode. A typical voltammograms of Cr(III) electroreduction are presented in Figure 3.



**Figure 3.** Typical series of voltammograms recorded on the lead electrode at different values of scan rate Chromium(III) methanesulphonate content is 0.005 M (green form) electrolyte contains 0.01 M MSA

The current peak corresponding to the electrochemical reaction (Eqn.1) appears at  $\sim -0.8$  to  $-1.0$  V (its precise position depends on the scan rate). Note that the current wave of Cr(III) ions reduction on Pb-electrode is not distorted by that corresponding to the HER.

An increase in potential scan rate causes the peak potential to shift cathodically. Such a type of behavior is typical of irreversible electrochemical process<sup>27,28</sup>. The following expression for the peak current of the one-electron irreversible electrochemical reaction is valid<sup>27,28</sup>.

$$i_p = 3,01 \cdot 10^5 \alpha^{1/2} D^{1/2} C_0 \nu^{1/2} \quad (2)$$

Where  $\alpha$  is the charge transfer coefficient,  $D$  is the diffusion coefficient,  $C_0$  is the depolarizer concentration in the bulk solution and  $\nu$  is the potential scan rate. On the other hand, another equation for the irreversible peak current was proposed<sup>29</sup>, which differs from Eqn. (2),

$$i_p = 0,23FC_0k_s \exp\left[-\frac{\alpha F(E_p - E^0)}{RT}\right] \quad (3)$$

Where  $E^0$  is the formal standard electrode potential,  $k_s$  is the standard rate constant,  $R$  is the universal gas constant,  $T$  is the temperature and  $F$  is the Faraday constant. According to literature<sup>27,28</sup>, the peak potential  $E_p$  is given by

$$E_p = E^0 - \frac{RT}{\alpha F} \left[0,78 - \ln k_s + \ln \sqrt{Db}\right] \quad (4)$$

$$\text{where, } b = \frac{\alpha F}{RT} v$$

When processing experimental data, the charge transfer coefficient  $\alpha$  was drawn out from Equation (4) by plotting  $E_p$  vs.  $\ln v$ . Then the value of the diffusion coefficient  $D$  was calculated on the basis of Equation (2) by linearizing the experimental data in the coordinates  $i_p$  vs.  $v^{1/2}$  (at constant value of  $C_0$ ) and (or)  $i_p$  vs.  $C_0$  (at constant value of  $v$ ). Finally, since  $E^0$  is not accurately known for the different Cr(III) complexes under study, the standard rate constant  $k_s$  as well as the formal standard electrode potential  $E^0$  were determined solving simultaneous Equations (3)-(4) using preliminarily determined values of  $\alpha$  and  $D$ .

It must be stressed that the linear characters of dependences in the coordinates  $E_p$  vs.  $\ln v$ ,  $i_p$  vs.  $v^{1/2}$  (at  $C_0 = \text{const}$ ) and  $i_p$  vs.  $C_0$  (at  $v = \text{const}$ ) confirm the applicability of Eqs. (2)-(4) to the electrochemical system under question. The calculated kinetic parameters of electrochemical reaction (1) are given in Table 1.

**Table 1.** Kinetic and thermodynamic data for the one-electron reduction of Cr(III) complexes on Pb electrode

Kind of Cr(III) complex	$\alpha$	$k_s, \text{cm s}^{-1}$	$E^0, \text{V}$
Cr(ClO <sub>4</sub> ) <sub>3</sub> (aqua-complex)	0.49	$6.09 \cdot 10^{-4}$	-0.493
Cr(MS) <sub>3</sub> (violet form)	0.49	$9.16 \cdot 10^{-5}$	-0.498
Cr(MS) <sub>3</sub> (green form)	0.50	$3.13 \cdot 10^{-5}$	-0.505
Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (green form)	0.49	$2.57 \cdot 10^{-5}$	-0.516

As can be seen, all calculated transfer coefficients  $\alpha$  are close to 0.5. The standard rate constant for the discharge of violet Cr(III)-MSA complexes is somewhat less than that obtained for aqua-complexes. This fact confirms additionally the conclusion about formation of Cr(III)-MSA complexes. Conversion of the violet Cr(III)-MSA complex into the green form leads to a decrease in the value of standard rate constant which may be caused by complication of Cr(III) complexes structure (their polymerization).

Some variation of the formal standard electrode potentials reflects possible changes in the Cr(III) complexes stability constants. Let us note that the formal value of  $E^0$  for the green form of MSA complex is more negative than that peculiar to the violet form.

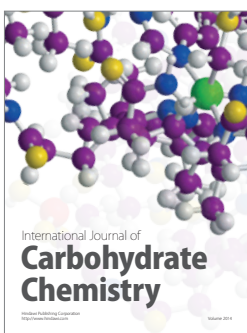
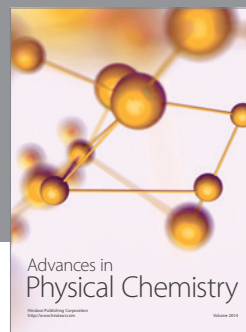
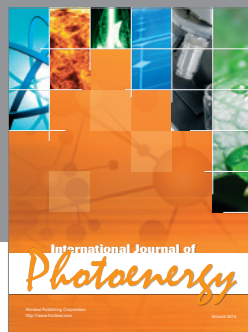
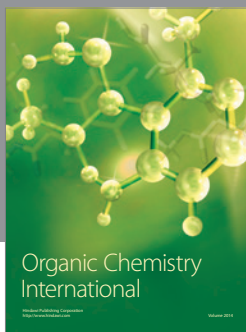
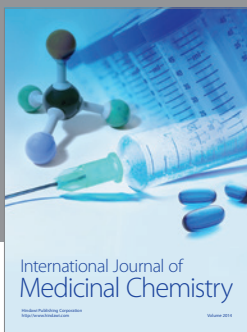
## Conclusion

1. Trivalent chromium ions were stated to exist in methanesulphonate aqueous solutions both in a violet form and in a green one. Transformation of a violet form of Cr(III)-MSA complexes into a green one may be related with polymerization and formation of polynuclear complexes containing sulfato-, ol-, oxo-bridges.

2. The Cr(III) electroreduction process on lead electrode is irreversible in electrolyte containing MSA. The standard rate constants of the Cr(III) discharge diminish in the following sequence: Cr(ClO<sub>4</sub>)<sub>3</sub> (aqua-complex) – Cr(MS)<sub>3</sub> (violet form) – Cr(MS)<sub>3</sub> (green form) – Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (green form).

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