



**M.V. Lomonosov Moscow State Academy  
of Fine Chemical Technology**

Department Chemistry and technology of rare elements  
and materials for electronic technique



## **Electrochemical synthesis of rhenium oxo- and oxoalkoxoderivatives.**

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### **Objects of the research:**

- *The investigation of how different electrochemical parameters influence on the process and the result of rhenium anodic dissolution .*
- *Determination of possible ways of rhenium alkoxide formation during the electrolysis.*

# Synthesis of rhenium alkoxides

## *Ligand substitution technique* *Methods with the use of rhenium(VII) oxide* **Electrochemical method**

Factors influencing on rhenium anodic dissolution:

- electrochemical parameters (potential, voltage, current density)
- temperature
- nature and concentration of background electrolyte
- alcohol composition
- construction of electrochemical cell
- purity of anode
- secondary chemical processes occurring in a bulk (reactions of alkoxide association, etc.)

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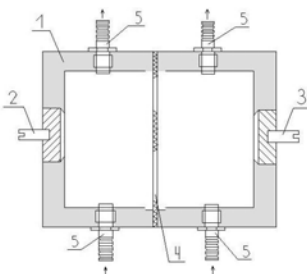
# Equipment

Electrochemical cell for synthesis of alkoxoderivatives:

- 1 – cell body;
- 2 – titanium cathode;
- 3 - anode (Re);
- 4 – membrane MK-40;
- 5 – connector;

$V_{\text{electrolyte}} = 100 \text{ ml}$

$C(\text{LiCl}) = 0,05\text{-}0,06 \text{ mole/l}$



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## Experiment I, electrochemical synthesis under the fixed potential $E = 2,910 \pm 0,007V$

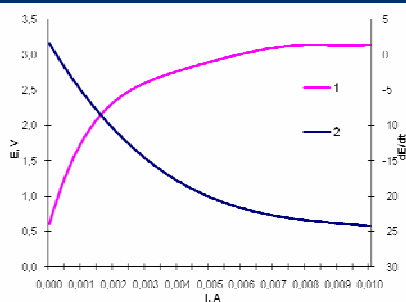


Fig. 1. Dependence of anodic potential  $E$  (curve 1) and rate of potential varying  $dE/dt$  (curve 2) on current at random flow of electrolyte.

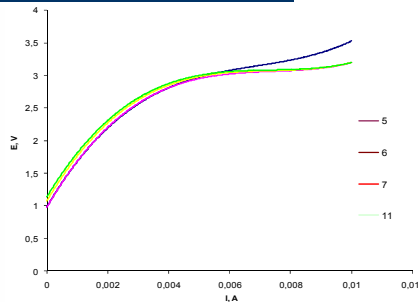


Fig. 2. Anodic polarization curves at different rate of electrolyte.

$E = 2,910 \pm 0,007V$   
 $T = 20-25^{\circ}C$   
 $V_{\text{electrolyte}} = 0,4 \text{ л/ч}$   
 $U < 20V$

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## The electrochemical complex



Fig. 3. The electrochemical complex

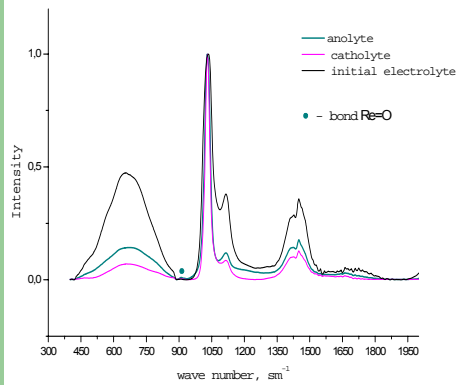
The electrochemical complex is developed, in which it is used by a direct (not compensatory) a way of measurement of potential of an electrode.

The electrochemical complex has the high accuracy of measurements and allows to receive the additional information on object of researches (speed of change of potentials, points of change of electrochemical reactions, etc.)

The electrochemical complex allows to carry out the integrated technological experiences. The complex may be used in the industry as intellectual self-adapting electrochemical unit for carrying out of wide technological processes.

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## IR-spectroscopy



Bond	Wave number, $\text{cm}^{-1}$
Re=O	915 – 909
Re-OR, Re-O(R)-Re	524
Re-O(R)	520
Re-O-Re	850
C-O alcohol	1158, 1019

Table 1. Literary data on IR-spectroscopy.

Fig. 4. IR-spectra of anolyte, catholyte and initial electrolyte at  $E = 2,910 \pm 0,007\text{V}$ .

Rhenium concentration:  
in anolyte – 0,38 g/l; in catholyte – 0,42 g/l

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## ESR-spectroscopy

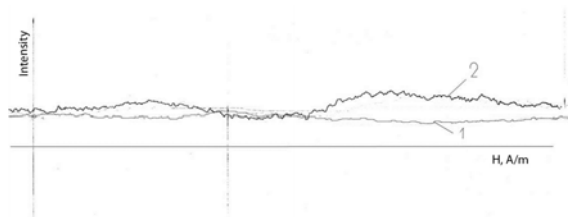


Fig. 5. ESR-spectra of anolyte (1) and catholyte (2) at  $E = 2,910 \pm 0,007\text{V}$ .

$$n = M \cdot Q / (m \cdot F) = 186,2 \cdot 145,45 / (0,04 \cdot 96500) = 7,02$$

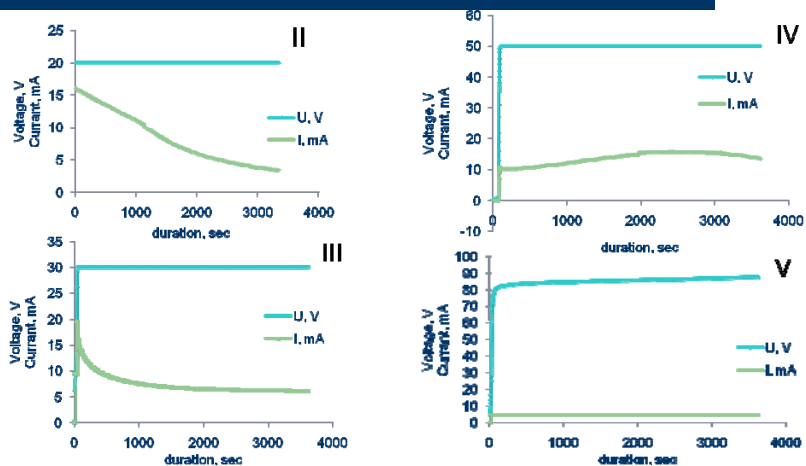
where  $n$  is an oxidation number;  $M$  is molar mass;  $Q$  is a quantity of electricity;  $m$  is the mass of dissolved rhenium; and  $F$  is Faraday constant.



Rhenium concentration: in anolyte – 0,38 g/l; in catholyte – 0,42 g/l

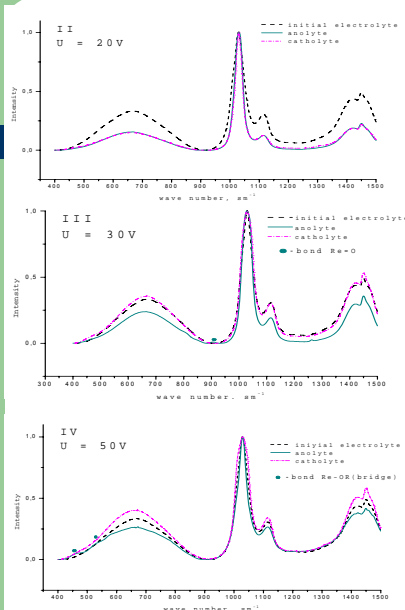
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## Changing of current and voltage during the process



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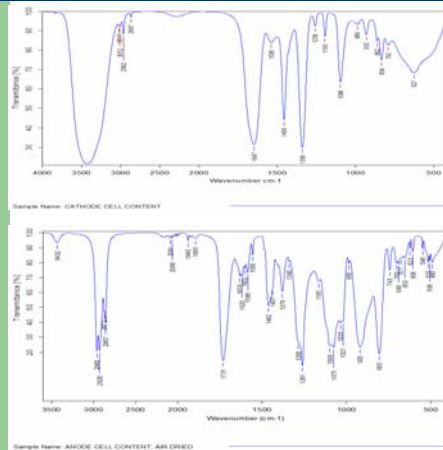
## IR-spectra of anolyte, catholyte and initial electrolyte at U = 20, 30, 50 V



№	Correlation of frequencies (sm <sup>-1</sup> ):	
	catholyte	anolyte
II	v O-H = 3327-3469 v C-O = 1031-1130 v C-H = 2819-2990 v Re=O = v Re - O (bridge) = 833 v Re - O(R) = 466-546	v O-H = 3327-3469 v C-O = 1031-1130 v C-H = 2819-2990 v Re=O = v Re - O (bridge) = 833 v Re - O(R) = 466-546
III	v O-H = 3223-3483 v C-O = 1033-1137 v C-H = 2821-2994 v Re=O = v Re - O (bridge) = (812-862) v Re - O(R) = 462-468	v O-H = 3223-3483 v C-O = 1033-1137 v C-H = 2821-2994 v Re=O = 909 v Re - O (bridge) = 812-862 v Re - O(R) = 462-468
IV	v O-H = 3236-3476 v C-O = 1034-1140 v C-H = 2822-2987 v Re=O = v Re - O (bridge) = (718) v Re - O(R) = (477)	v O-H = 3294-3409 v C-O = 1034-1140 v C-H = 2822-2987 v Re=O = v Re - O (bridge) = 718 v Re - O(R) = 458-579

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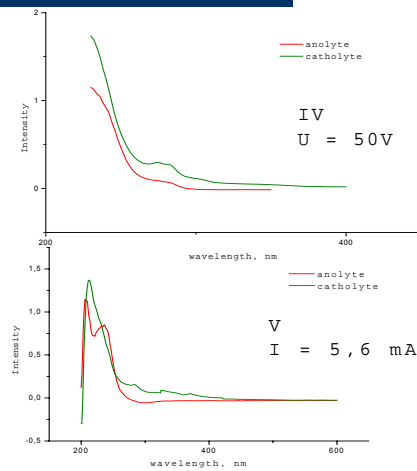
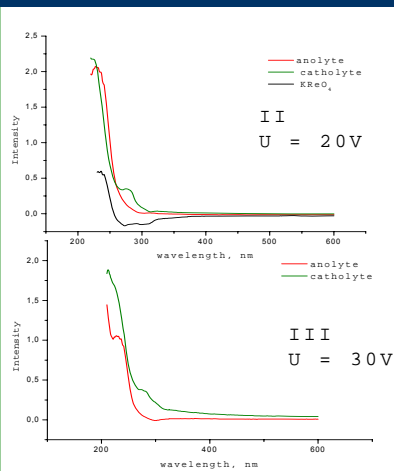
**IR-spectra of solid residue from anolyte (lower) and catholyte (higher), taken after evaporation of liquid at room temperature. Spectra are corrected by subtraction of watered LiCl.**



Correlation of frequencies (sm <sup>-1</sup> ):		
	catholyte (higher)	anolyte (lower)
v	v O-H = 3427	v O-H = 3432
	v C-O = 1077-1195	v C-O = 1031-1130
	v C-H = 2962-3016	v C-H = 2857-2960
	v Re-O = 932	v Re-O = 985
	v Re - O (bridge) = 862	v Re - O (bridge) = 899
	v Re - O(R) = (627)	v Re - O(R) = 548

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## Electron absorption spectra



Nº Exp.	Electrolysis parameters	$C_{\text{Re}}$ (catholyte), g/l	$C_{\text{Re}}$ (anolyte), g/l	Bond (caatholyte)	Bond (anolyte)
I	$E = 2,910 \pm 0,007\text{V}$ $U < 24\text{ V}$	0,42	0,38	Re=O, Re-OR Re - O (bridge)	Re=O, Re-OR Re - O (bridge)
II	$U = 20\text{ V}$	0,04	0,55	Re-OR Re - O (bridge)	Re-OR Re - O (bridge)
III	$U = 30\text{ V}$	0,30	3,27	Re-OR Re - O (bridge)	Re=O, Re-OR Re - O (bridge)
IV	$U = 50\text{ V}$	0,08	0,85	Re-OR Re - O (bridge)	Re-OR Re - O (bridge)
V	$I = 5,6\text{ mA}$	~0	4,39	(Re-OR) Re - O (bridge)	Re=O Re-OR Re - O (bridge)

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## Possible mechanism of rhenium anodic dissolution

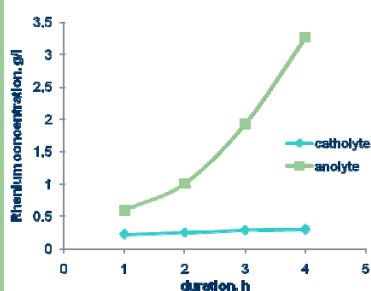
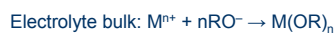
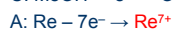
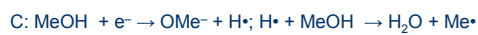
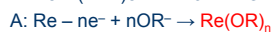
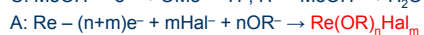
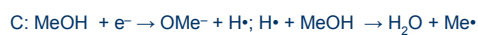


Fig. 7. Changing of rhenium concentration in electrolyte during the process (in catholyte and anolyte) at  $U = 30\text{ V}$ .

$$E = 2,910 \pm 0,007\text{ V}$$

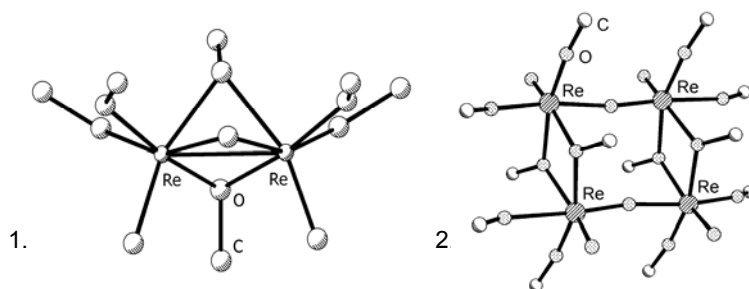


$$U = 20, 30, 50\text{ V}; I = 5,6\text{ mA}$$



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## Structures of rhenium methylates



Structures of alkoxoderivatives: 1 –  $\text{Re}_2\text{O}_3(\text{OMe})_6$ ; 2 –  $\text{Re}_4\text{O}_6(\text{OMe})_{12}$

(Shcheglov P.A., Drobot D.V. Reviews, Rhenium alkoxides // Russian Chemical Bulletin, International Edition. October 2005. v. 54, № 10, p. 2247-2258)

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## Conclusions:

- The influence of electrode potential on rhenium anodic dissolution has been studied. At fixed potential  $E = 2,91 \pm 0,07\text{V}$  ( $U < 24\text{ V}$ ) anodic oxidation of rhenium takes place, most probably, with the formation of  $\text{Re}^{7+}$  cation as follows:  
 $\text{A: Re} - 7\text{e}^- \rightarrow \text{Re}^{7+}$   
 Electrolyte bulk:  $\text{M}^{n+} + n\text{RO}^- \rightarrow \text{M}(\text{OR})_n$   
 (confirmed by IR and ESR spectral methods and the results of theoretical calculation)
- The influence of voltage and current on rhenium anodic dissolution has been studied. At fixed voltage  $U = 20, 30, 50\text{V}$ , and fixed current  $I = 5,6\text{ mA}$  ( $U > 80\text{V}$ ) rhenium occurs mostly in the form of anion or neutral molecule, probably,  $\text{Re}_x\text{O}_y(\text{OR})_n$ . The most expectable mechanism of rhenium anodic dissolution:  
 $\text{A: Re} - \text{ne}^- + n\text{OR}^- \rightarrow \text{Re}(\text{OR})_n$

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### The speaker is grateful to

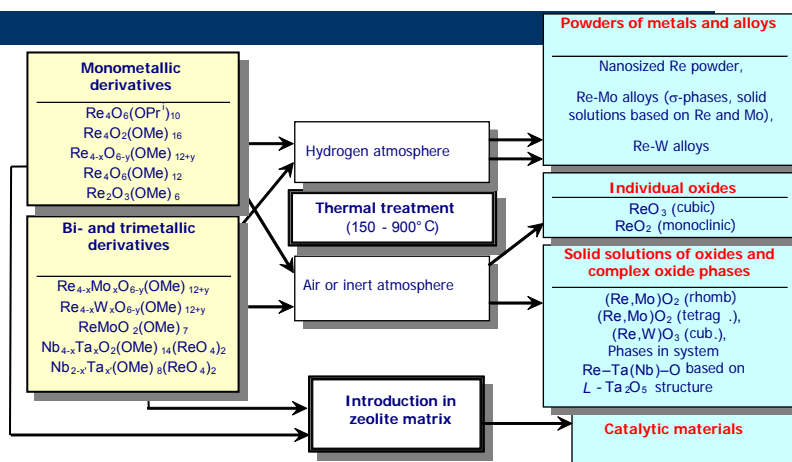
O.V. Chernyshova<sup>1</sup>, D.V. Drobot<sup>1</sup>, V.V. Kravchenko<sup>1</sup>, V.V.  
Minin<sup>2</sup>, A.N. Shchegolihin<sup>3</sup>

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Academy of Sciences  
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## Electrochemical synthesis of rhenium oxo- and oxoalkoxoderivatives.

E.N. Pryamilova, O.V. Chernyshova, D.V. Drobot  
Application of rhenium alkoxides:



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1. Shcheglov P.A., Drobot D.V. Rhenium alkoxides / Известия Академии Наук. Серия химическая, 2005, №10, p. 2177-2188.

## Методы получения алкокси- и оксоалкоксopроизводных рения:

### 1. Метод замещения лигандов:

#### Исходные соединения:

- амидные комплексы
- галогенидные комплексы
- оксогалогенидные комплексы

#### Алкоксилирующий реагент:

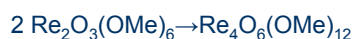
- спирты
- алкоголяты щелочных металлов
- алкоксopроизводные кремния



### 2. Реакция с участием оксида рения (VII):



### 3. Реакция ассоциации:



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## Анодное растворение рения в метаноле.

Shcheglov P.A. Drobot D.V. Reviews, Rhenium alkoxides // Russian Chemical Bulletin, International Edition. October 2005. v. 54, № 10, p. 2247-2258.

комплекс	условия электролиза
$\text{Re}_4\text{O}_2(\text{OMe})_{16}$ (Re V)	без разделения катодного и анодного пространств, повышенные значения катодной плотности тока Катод – Pt, анод – Re Электролит: MeOH, LiCl U=31,4 – 11,0 В; I=0,16 – 0,12 А jа=0,1 – 0,2 А/см <sup>2</sup>
$\text{Re}_4\text{O}_{6-y}(\text{OMe})_{12+y}$ (Re V,VI)	без разделения катодного и анодного пространств Катод – нержавеющая сталь, анод – Re Электролит: MeOH, LiCl U=110 В; I=1 А jа=0,56 А/см <sup>2</sup>
$\text{Re}_4\text{O}_6(\text{OMe})_{12}$ (Re VI)	с разделенным катодным и анодным пространствами Катод – Pt, анод – Re Электролит: MeOH, LiCl U=25 В; I=0,055 А jа=0,01 – 0,02 А/см <sup>2</sup>

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## Механизм анодного растворения металла в спирте в присутствии фонового электролита

- |  |  |
|--|--|
| <p>1.<br/> <math>\text{ROH} \rightarrow \text{OR}^- + \text{H}^+</math><br/>                 К: <math>\text{H}^+ + \text{e}^- \rightarrow 1/2\text{H}_2</math><br/>                 А: <math>\text{M} - \text{ne}^- \rightarrow \text{M}^{n+}</math><br/>                 Объем электролита: <math>\text{M}^{n+} + \text{nRO}^- \rightarrow \text{M}(\text{OR})_n</math></p>   | <p>3.<br/>                 А: <math>\text{M} - (\text{n+m})\text{e}^- + \text{mHal}^- + \text{nOR}^- \rightarrow \text{M}(\text{OR})_n\text{Hal}_m</math><br/>                 К: <math>\text{M}(\text{OR})_n\text{Hal}_m + \text{me}^- \rightarrow \text{M}(\text{OR})_n + \text{mHal}^-</math><br/>                 Объем электролита:<br/> <math>\text{M}(\text{OR})_n + \text{mROH} \rightarrow \text{M}(\text{OR})_{\text{n+m}} + \text{m}/2\text{H}_2</math></p> |
| <p>2.<br/>                 А: <math>\text{Hal}^- - \text{e}^- \rightarrow \text{Hal}\cdot</math>; <math>\text{M} + \text{nHal}\cdot \rightarrow \text{MHal}_n</math><br/>                 К: <math>\text{MHal}_n + \text{pe}^- \rightarrow [\text{MHal}_n]^{n-}</math><br/>                 Объем электролита:<br/> <math>[\text{MHal}_n]^{n-} + \text{nHOR} \rightarrow \text{n}/2\text{H}_2 + \text{nHal}^- + \text{M}(\text{OR})_n</math></p> | <p>4.<br/>                 К: <math>\text{ROH} + \text{e}^- \rightarrow \text{OR}^- + \text{H}\cdot</math><br/>                 А: <math>\text{M} - \text{ne}^- \rightarrow \text{M}^{n+}</math><br/>                 Объем электролита: <math>\text{M}^{n+} + \text{nOR}^- \rightarrow \text{M}(\text{OR})_n</math></p>   |

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## Теоретический расчет

Концентрация рения определена согласно фотометрической методике:  
 анолит – 0,38 г/л; католит – 0,42 г/л

**Расчет**, косвенно определяющий степень окисления рения в растворе анолита:

Данные:

- концентрация рения по данным фотометрического анализа в анодной ( $C_1$ ) и катодной ( $C_2$ ) частях объемом по 50 мл каждая:  $C_1 = 0,38\text{ г/л}$  и  $C_2 = 0,42\text{ г/л}$ ;
- количество пропущенного электричества  $Q = 145,45\text{ А}\cdot\text{с}$ ;
- молярная масса рения  $M = 186,2\text{ г/моль}$ ;
- число Фарадея  $F = 96500\text{ г/(А}\cdot\text{с)}$

Закон Фарадея при 100% выходе по току:  $m = \frac{Q \cdot M}{n \cdot F}$

где  $n$  – степень окисления иона,

$m$  – масса растворившегося рения.

$$m = m_1 + m_2 = C_1/V_1 + C_2/V_2 = 0,38/0,05 + 0,42/0,05 = 0,04\text{ (г)}$$

$$n = M \cdot Q / (m \cdot F) = 186,2 \cdot 145,45 / (0,04 \cdot 96500) = \underline{7,02}$$

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## Механизм анодного растворения металла в спирте в присутствии фонового электролита

1. Прямой электрохимический синтез алколюатов металлов // Изв. АН СССР, сер. хим. 1981. №8, с. 1687-1692.



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## Механизм анодного растворения металла в спирте в присутствии фонового электролита

2. Прямой электрохимический синтез алколюатов металлов // Изв. АН СССР, сер. хим. 1981. №8, с. 1687-1692.



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## Механизм анодного растворения металла в спирте в присутствии фонового электролита

3. Прямой электрохимический синтез алколюатов металлов // Изв. АН СССР, сер. хим. 1981. №8, с. 1687-1692.



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## Механизм анодного растворения металла в спирте в присутствии фонового электролита

4. Катодное расщепление связи О-Н. Электрохимическое восстановление алифатических спиртов и фенола // ЖОХ. 1986. т. 56, № 6. с. 1356-1360.



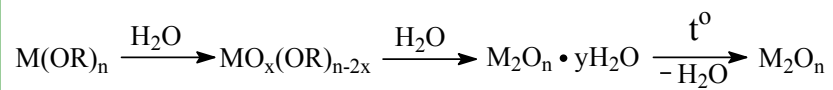
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## Авто-диссоциация метанола



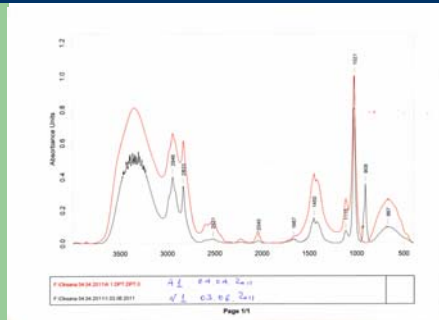
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## Золь-гель технология

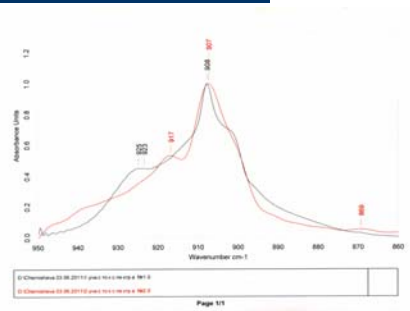


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## ИК-спектры. E = 2,910В



**Рис. 1.** ИК-спектры концентрированных растворов католита (красный) и анолита (черный).



**Рис. 2.** ИК-спектры концентрированного раствора анолита (черный) и исходного раствора анолита (красный).