

# Improving the catalytic activity of nickel-containing anodes for the oxidation of alcohols

## The industrial electrosynthesis of diaceton-2-keto-L-gulonic acid

Victor G. Mairanovsky · Isaac G. Gitlin ·  
Sergej A. Rosanov

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**Abstract** Looking for ways to improve the catalytic activity of a Ni anode during the oxidation of alcohols in basic medium, we tested the action of amino compounds as Ni-complexing agents. We have discovered a significant increase in the effective rate of oxidation of alcohols to the corresponding carboxylic acids in the presence of amino compounds. The activating effect of amino compounds (AEAC) became the basis for the industrial method to produce the carboxylic acid diaceton-2-keto-L-gulonic acid (DAG), an intermediate in the synthesis of vitamin C. The DAG electrosynthesis at stainless steel (StS) anodes with a capacity of 1,500 t/year/production line was developed. The application of the electrochemical method allowed drastically reducing the wastes and resulted in significant economy effects. Operation during 10 years showed good anode corrosion resistance, stability, and safety of the process. There are other possible AEAC applications, in particular, for increasing the sensitivity of ROH sensors. The possibility of using the

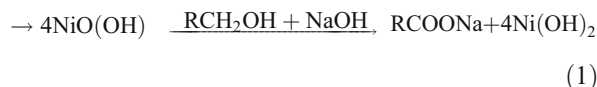
AEAC effect for improving the efficiency of direct alcohol fuel cells (DAFC) with Ni-containing systems is also discussed.

**Keywords** Nickel-containing anode activation · Alcohol oxidation · Industrial electrosynthesis · Carboxylic acid electrosynthesis · Diaceton-2-keto-L-gulonic acid · Electrocatalysis

### Introduction

The electrocatalytical oxidation of alcohols, in particular, of the group of carbohydrates, leading to carboxylic acids attracted a lot of attention. One of the commonly used methods for the implementation of the process is based on the use of Ni anodes in alkaline media. Such a process, the foundations of which have been established by the groups of Vertes [1, 2] and Fleischmann [3], can be formulated as follows:

Anode:



Cathode:



Here, RCH<sub>2</sub>OH and RCOONa are alcohols and carboxylic acids (Na salt), respectively; Ni(OH)<sub>2</sub> and NiO(OH) are

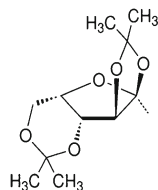
V. G. M. dedicates this publication to Dr. Nina Fjodorovna Zakharchuk on the occasion of her 75th birthday.

V. G. Mairanovsky (✉)  
Scientific Society WiGB,  
Oranienburger Str. 31,  
10117 Berlin, Germany  
e-mail: vmairan@gmx.de

I. G. Gitlin  
NPK ECHO,  
Butlerova ul. 17,  
117342 Moscow, Russia

S. A. Rosanov  
PIK Pharmachim,  
Raboehaja ul. 14,  
308013 Belgorod, Russia

the reduced and oxidized (active) forms of the catalyst. Actually, the oxidized form consists of  $\beta$ ,  $\gamma$  modifications with different oxidation states of Ni, up to  $\sim 3.7$  for the  $\gamma$  modification [4–6]. The method is very attractive for industrial application because of its high yield. Thus, in one of the first works [2] diacetone-L-sorbose (DAS) was tested as  $RCH_2OH$ , since it is an intermediate in the production of ascorbic acid (vitamin C) by the Reichstein method [7]; the world's annual production of ascorbic acid is many thousands of tons. Here R is:



and the product is diaceton-2-keto-L-gulonic acid (DAG).

However, the industrial implementation of an electrochemical oxidation of alcohols according to Reaction 1 faces some severe problems:

- (i) Passivation, i.e., deactivation of the Ni anode occurs rather fast, especially when performing the process under industrial conditions (technical-grade substances, etc.).
- (ii) The target Reaction 1 and the side Reaction 2 of the oxygen evolution take place at close potentials, and the product ratio is determined by the kinetics of chemical stages of Reactions 1 and 2.

The first problem (passivation), as shown by Fioshin et al. [8, 9], is solved by adding catalytic amounts of nickel salts to the electrolyte. Such composition, electrolyte NaOH + Ni<sup>2+</sup>, was used in the small-scale, 250 t/year DAG production at graphite anodes [10]. The second circumstance leads to the need to work at very low current densities [3]. Otherwise, current efficiencies are not high enough: typically 30–50 %, even when using modern anode materials, such as Ni foams [11–13] with the special cell [12, 13]. The decrease of the current density leads to the corresponding reduction in productivity; the necessary capacity is provided then by increasing the anode surface area [14–18].

We attempted to find another solution, namely, to find an activator (A) for the target Reaction 1. Starting from the assumption that the nickel complexation can positively affect the catalytic activity in the oxidation process, we studied the effect of amino compounds as complexing agents.

Here, we report on the use of this approach in the development of large-scale electrosynthesis of the carboxylic acid, DAG, instead of the previously existing technology with the use of potassium permanganate. The work was undertaken in the Physical Chemistry lab of All Union

Research Vitamin Institute, Moscow, in conjunction with the Department of the Chief Engineer of the Joschkar-Ola Vitamin plant. The results which we report in this paper could not be published for many years because of confidentiality restrictions.

## Experimental

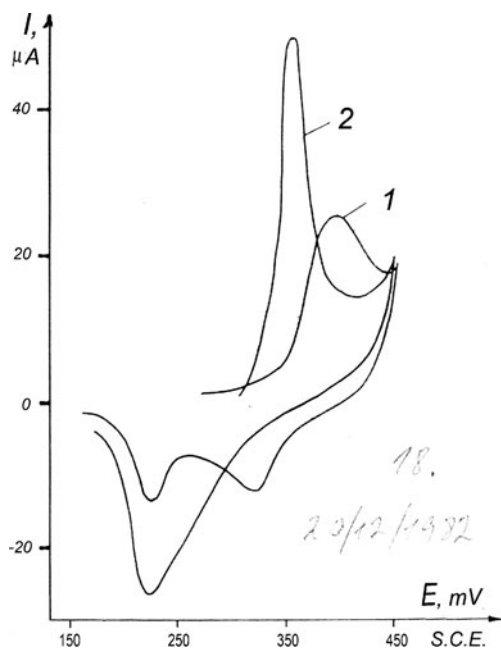
Cyclic voltammetry, rotating disc electrode (RDE) voltammetry and galvanostatic preparative electrolysis were applied in the laboratory research. Standard equipment was used: potentiostat PAR-173 and generator PAR-175 (Princeton Applied Research), RDE device Tacussel with a speed control unit. For the RDE voltammetry, electrodes with an electrode surface area of  $A=0.9 \text{ cm}^2$  were made of the corresponding materials, thus Ni 99.98 % or stainless steel (StS) 12XI8H10T. The electrodes have been polished with an abrasive paste for voltammetry additionally with diamond paste.

For preparative electrolysis, a set of eight uniform stirred cells with StS electrodes of  $A=9.0 \pm 0.3 \text{ cm}^2$  was used. The cells were equipped with autonomous power sources (TEC-13 stabilized controlled current sources). Under identical electrolysis conditions, the process rates differed in the cells by not more than 7 %. All experiments were carried out with thermostatic control (temperature range 20–70 °C, ultrathermostat U1, VEB Prüfgerätewerk, GDR). In the laboratory experiments, refined DAS, NaOH (p.a.), and NiSO<sub>4</sub> “without cobalt” were used. In order to ensure operative analytical control, an express method of polarimetric determination of DAG in the presence of DAS was developed [19].

## Results

In initial experiments, with nickel as an anode material, some short primary aliphatic alcohols were examined. The results were in good agreement with those obtained by Fleishmann et al. We studied the effect of amino compounds as activators (see “Introduction”). The first voltammetric experiments with the addition of ammonia showed a critical change: a significant increase in the anodic peak and its shift to lower potentials, disappearance of the cathodic peak related to the reduction of  $\gamma$ -NiOOH (cf. [5]), and, conversely, the increase in the cathodic peak, related to the reduction of  $\beta$ -NiOOH (Fig. 1).

As a result of the following experiments, it was really found that the rate of the electrocatalytical oxidation  $RCH_2OH \rightarrow RCOOH$  significantly increased in comparison to the oxygen evolution in the presence of those substances containing amino groups (activator A). Thus, it became



**Fig. 1** Cyclic voltammograms: Ni electrode,  $v=5$  mV/s, 0.05 M NaOH, 0.002 M NiSO<sub>4</sub>, 40 °C. 1 without NH<sub>3</sub>, 2 in the presence of 0.02 M NH<sub>3</sub>

possible to conduct the electrolysis with acceptable current efficiencies at current densities up to  $j=10\text{--}15$  A/dm<sup>2</sup>. The activating effect of amino compounds was confirmed during the oxidation of DAS [20, 21], even though the absolute value of the rate of oxidation is lower than that of short primary aliphatic alcohols (up to n-butanol).

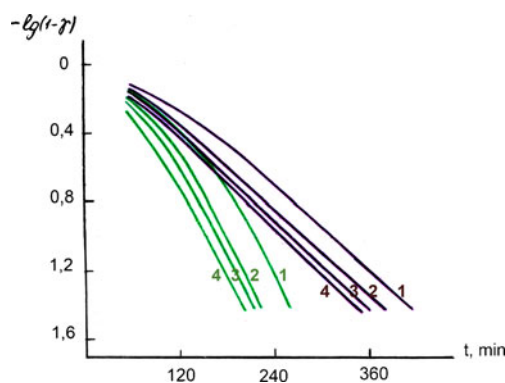
Facing the task of developing the industrial cell, we tested, during our next stage of work, the less rare and cheaper material stainless steel (StS, mark 12X18H10T, basic alloy with 11 % Ni, 17 % Cr, 2 % Mn, and 0.8 % Ti). In accordance with the low oxygen overvoltage in an alkaline medium for the Fe anode [22], the substitution of Ni by the StS anode is accompanied by a significant increase in the oxygen evolution current, and the anodic peak turns out to be poorly developed. Nevertheless, even under those circumstances, in the presence of an activator, we obtained an encouraging result: the coefficient  $K$  of linear dependence of  $i = Kc_{\text{ROH}}$  between current and the DAS concentration increased by more than two times in the presence of the activator (StS anode, RDE,  $\omega=200$  r/min,  $v=5$  mV/s, 1 M NaOH, 0.02 M NiSO<sub>4</sub>, activator Trilon B).

The process at the StS anode was optimized first under laboratory conditions. In the course of this, the substance concentrations (NaOH, DAS, NiSO<sub>4</sub>, and activator), the current density, the working temperature, and the presence of alien impurities were taken as variable parameters. The output parameters were: current efficiency  $\beta$ , substance yield  $\eta$ , productivity, passivation, and the corrosive wear of the anode. We selected ethylenediaminetetraacetate

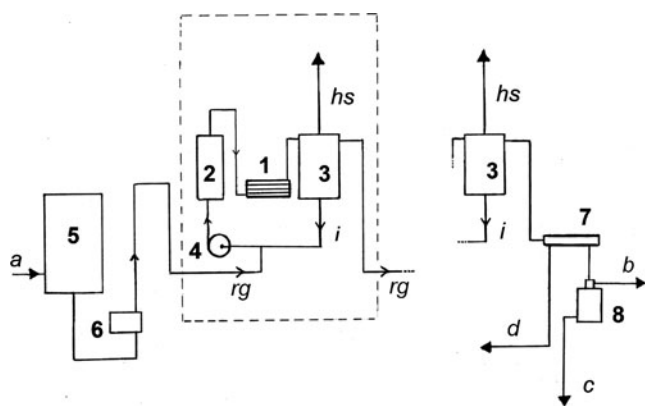
(disodium salt, Trilon B), a strong complexing agent, as activator A.

As an example, demonstrating the effect of the activator, Fig. 2 shows a series of kinetic curves obtained in preparative galvanostatic oxidation of DAS to DAG at the StS anode in the presence of 0.02 M NiSO<sub>4</sub> at 50 °C at several current densities for the conversion grade up to ~96 % ( $\gamma \sim 0.96$ ). The curves represent here the kinetics of the process after an additional short, approximately 1-h anodic activation during the electrolysis. In the conditions of the given experiment, for  $j=6\text{--}11$  A/dm<sup>2</sup>, the kinetic curves start satisfying curves of first-order reaction after passing of approximately 19 Ah/dm<sup>2</sup> and 23 Ah/dm<sup>2</sup>, in the absence and in the presence of 2 g/dm<sup>3</sup> of Trilon B, respectively. The addition of the activator significantly increases the process rate, providing also higher values of current efficiency  $\beta$ , i.e., there is a significant increase in the rate of the limiting chemical stage for the target Reaction 1 compared to the oxygen evolution Reaction 2. Thus, the degree of conversion 90 % ( $\gamma=0.9$ ) at the current densities  $j=6.7$  A/dm<sup>2</sup> in the presence of Trilon B is attained in 3.5 h at a current efficiency  $\beta=80$  %, whereas in its absence in 5.1 h at a current efficiency  $\beta=60$  %; at the current densities  $j=11.1$  A/dm<sup>2</sup>, respective magnitudes for  $\gamma=0.9$  are 2.5 h,  $\beta=70$  % and 4.0 h,  $\beta=40$  %.

Kinetic curves substantially change due to changes in the conditions of the electrolysis. The study of the dependence of the rate of electrooxidation and temperature revealed the existence of a smooth maximum around 50–60 °C becoming more pronounced with increasing concentration of NaOH (concentration range used is 0.3–2.0 M). A smooth maximum is also observed for the dependence of the process rate on the concentration of the activator ( $c_A=0.001\text{--}0.015$  M). An important observation made in the course of studying the impact of impurities is the significant inhibiting effect of cobalt(II) ions which manifests even at concentrations of  $\text{Co}^{2+} \leq 5$  %



**Fig. 2** Kinetics of the galvanostatic electrooxidation of diacetone-L-sorbose (0.46 M) at the stainless steel anode in the absence (brown) and in the presence (green) of the activator (2 g/dm<sup>3</sup> Trilon B). Electrolyte 0.7 M NaOH + 0.02 M NiSO<sub>4</sub>, temperature 50 °C. Curves 1–4 correspond to the current densities  $j=6.7, 7.8, 9.0,$  and  $11.1$  A/dm<sup>2</sup>, respectively



**Fig. 3** Electrochemical production of DAG, the dotted line shows a module unit: 1 electrolyzer, 2 cooler, 3 phase separator, 4 centrifugal pump, the first and the last modules are showed; 5 inlet reservoir; 6 dosing pump; 7 setting centrifuge; 8 separator. Lines a, b, c, and d correspond to the input of the initial solution DAS, the output of the solution DAG, exit the waste fine solid particles and solid product, basically  $\text{Ni}(\text{OH})_2$ , respectively (details in the text)

relative to the  $\text{Ni}^{2+}$  content; the inhibiting effect was not eliminated completely in the presence of an activator. Thus, in the process development nickel sulfate with the technical specification “without cobalt” was used.

The optimal conditions found in the laboratory were tested on an enlarged electrolyzer, which was supposed to form the base of the industrial device. For this, we chose a bipolar filter press cell with undivided anode–cathode spaces. The absence of a separating membrane reduces the electric resistance, simplifying the construction and the

exploitation of the apparatus. The enlargement of the cell had virtually no impact on the optimal conditions of electrolysis; thus, the initial concentrations are of  $\text{NaOH}$ : 38–42  $\text{g}/\text{dm}^3$ ,  $\text{DAS}$ : 110–140  $\text{g}/\text{dm}^3$ ,  $\text{Ni}_2\text{SO}_4$ : 3.2–5.2  $\text{g}/\text{dm}^3$ , Trilon B: 0.4–0.6  $\text{g}/\text{dm}^3$ , the initial current density was  $j=7\text{--}9 \text{ A}/\text{dm}^2$ , the end current density  $j=0.5\text{--}2 \text{ A}/\text{dm}^2$ , and the temperature range was 52–58 °C.

After carrying out several experimental electrolyses and some improvements of the electrolyzer design, a series of electrolyzers was manufactured (in the workshop of the Joschkar-Ola plant); to ensure regulated technological parameters 10 U were required. The electrolyzer is a rectangular horizontal unit (filter press bipolar cell), and the electrodes are made of 12XI8H10T StS plates 4 mm thick. Between the plates, along the contour, are rubber gaskets with fixing elements. The supporting elements made of Teflon were installed in the center; the working gap between the plates was 4 mm.

The production line was based on the module principle and consists of 10 similar units, each one including an electrolyzer, cooler, phase separator, and centrifugal pump (Fig. 3). The prepared initial solution was loaded into a reservoir and then carried to the first module. The pump provided a continuous circulation of the solution in the system (rg–i) electrolyzer–cooler phase separator; the dosing pump provided a non-stop solution feeding into each following module (it was fed to the suction line of the next centrifugal pump). The solution went out of the last module through the setting centrifuge (DAG finished solution, line b), whereas the separated solid product, basically  $\text{Ni}(\text{OH})_2$

**Table 1** Industrial electrocatalytic syntheses of diacetone-2-keto-L-gulonic acid (DAG)

Number	Parameter/developer	ETH Zürich and Hoffmann-La Roche [14, 15]	All-Union Research Vitamine Institut, Moscow and Joschkar-Ola Vitamin plant [20, 21, 23, 24]
1	Capacity, DAG, (t/year)	750 <sup>a</sup>	1,500 <sup>a</sup>
2	Regime	Continuous	Continuous
3	Electrolyzer	“Swiss-roll”, plastic isolating net	Bipolar filter press undivided cell
4	Anode material	Nickel foil	Stainless steel
5	Electrolyte	$\text{NaOH} + \text{Ni}^{2+}$	$\text{NaOH} + \text{Ni}^{2+} + \text{Trilon B}$
6	Current density for the 1st electrolyzer ( $\text{A}/\text{dm}^2$ )	0.4 <sup>b</sup>	7.0
7	DAG—productivity ( $\text{kg}/\text{m}^2 \text{ h}$ )	0.043 <sup>b</sup>	1.1
8	DAG—isolated yield ( $\eta$ , %)	93 <sup>b</sup>	93
9	Residual DAS ( $\text{g}/\text{dm}^3$ )	No data	2.0
10	Current efficiency ( $\beta$ , %)	70 <sup>b</sup>	70
11	Corrosion resistance of the anodes	Tolerable <sup>b</sup>	Very high
12	The operation period	No data	10 years <sup>c</sup>

<sup>a</sup> Capacity per one line

<sup>b</sup> Minipilot electrolysis data [14, 15]

<sup>c</sup> The process was stopped in 1994 due to the cessation of production of vitamin C at the Joschkar-Ola plant

was returned into the process after the regeneration, line d; nickel sulfate was added to the solution as appropriate. The monitoring of the process was carried out by measuring the steady-state concentrations DAG (see “[Experimental](#)”). The waste fine solid particles went by the line c, separator. The gaseous products from each phase separator escaped right into the atmosphere (line hs), and the phase separator filling coefficient by the liquid phase was always close to 1. These measures have been taken to ensure the safety of production (undivided electrolyzers, the formation of H<sub>2</sub> and O<sub>2</sub>, and Reactions 3 and 2). There was a bypass line in the system (not shown in the figure) which allowed disconnection from any module, e.g., for repair, without production stop.

The process was commissioned at the Joshkar-Ola plant without interrupting the running production of ascorbic acid, and its parameters are given in Table 1. Here are also given the parameters of the “low-current densities” technology, offered at Hoffmann La Roche [14, 15]: reduced productivity is compensated in this case using special Swiss-roll cell with large surface area. This cell, developed by Robertson et al. [16, 17], is comprised of two bands (anode and cathode) of Ni foil with a ~1 mm thick isolating plastic net, rolled into a cylindrical StS steel container; in a series, several such cells are used [14, 15].

The DAG synthesis became the greatest organic electro-synthesis realized in the USSR/Russia. Capacity of the electrosynthesis can be extended further several times by increasing the number of lines. The application of the electrochemical technology allowed drastically reducing the wastes and resulted in a significant economic effect. Ten years operation showed a good reliability, stability, and safety of the process. It also turned out that the use of the activator leads to a significant decrease in the rate of corrosive wear of the anode (practically absence of corrosion).

## Conclusion

We have presented results of experiments showing significant increase in the activity of the nickel-containing anode in alkaline media in the presence of amino compounds. Based on this finding, we have developed an effective, large-scale electrosynthesis of carboxylic acid, DAG, the intermediate in vitamin C production, from the corresponding alcohol, with the use of StS anode.

The role of the anode material composition and mechanism of the activating action of amino compounds had not been the subject of study in this work. The effect of the composition of the Ni-containing catalyst and its preparation method on the alcohol oxidation kinetics was under investigation in recent years [25–30]. In particular, it was found that the addition of iron to the Ni-Pd/Cu system leads to an increase in catalytic activity for oxidation of ethanol (bi-functional effect of Ni and Fe) [27].

Obviously, amino compound as a complexing agent is involved in the formation of the active surface layer: this is supported by an increase in duration of the activation period in the presence of Trilon B (Fig. 2) by an extremum-type dependence of the oxidation rate on the Trilon B concentration (further increase in the layer thickness results in a decrease in the ROH oxidation rate). Finally, element analysis showed the presence of nitrogen in the surface layer after electrolysis. To clarify the mechanism of the activation by the amino compounds and to study the active layer structure, combined electrochemical techniques such as in situ FTIR, SEM, STM, AFM, etc., deserved to be applied. The use of complex-forming reagents to achieve a catalytically active surface of the nickel-containing anode is an intriguing problem here.

Alongside preparative objectives, i.e., the effective synthesis of carboxylic acids from corresponding alcohols, both in the laboratory and on a large scale, the activating effect of amino compounds may be also used for other purposes, in particular, to increase the sensitivity of the alcohol sensors (cf. RDE voltammetric data, previous section). The activation by amino compounds may prove to be useful for the development of direct alcohol fuel cells (DAFC) [31]. Under certain conditions, Ni-containing systems (Pt/Ni, Pd/Ni, etc.) assure a deep oxidation of alcohols with C–C bonds rupture, up to CO<sub>2</sub> [32], and the removal of kinetic limitations of chemical stages is here the key problem.

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