Direct Electrochemical Synthesis of Metal Alkoxides

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The wide applications of metal alkoxides, in particular in the preparation of various industrial oxide materials, make the development of improved techniques for their production an urgent task. The current methods of synthesis of $M(OR)_n$ where n exceeds 2 are mostly based on exchange reactions between MX_n (X may be Hal, R, H, NR_2, $N(SiMe_3)_2$, *etc.*) and alkoxidizing reagents [1]. These reactions are multistep processes and the starting materials are difficult of access. In addition, they involve various by-processes which contaminate the products and decrease their yields.

For these reasons, the direct electrochemical synthesis of metal alkoxides by anode dissolution of metals in absolute alcohols in the presence of a conductive admixture seems a very promising method. Since Szilard showed the possibility, in principle, of preparing copper and lead alkoxides by electrolysis of methanol solutions of sodium methoxide in 1906 [2], only in recent years have a number of publications (mostly patents) appeared on the electrochemical synthesis of some metal alkoxides [3–8].

Lehmkuhl *et al.* [4–6] described the cathodic formation of Fe, Co and Ni alkoxides ($M(OR)_2$, where R is Me, Et, tert- and n-Bu) with the use of LiCl or NaBr as conductive admixtures. The preparation of Si, Ti, Ge, Zr and Ta ethoxides in the electrolysis of saturated alcoholic solutions of NH_4Cl was patented. The process was reported to cease after several hours [7, 8].

In this work, the major factors governing the electrochemical synthesis of metal alkoxides have been studied and the range of applicability of the procedure has been determined.

The electrolysis was run under argon in a cylindrical 80 ml volume glass cell without separating the cathode and anode spaces. The cell was equipped with a reflux condenser, a magnetic stirrer, an anode of 1 to 5 cm^2 area made of the corresponding metal and a platinum cathode (2 cm^2 area).

Metal alkoxides formed in the electrochemical reaction in the crystalline form were separated from the mother liquor and recrystallized from the alcohol. Metal alkoxides liquid at room temperature were isolated by distillation under vacuum.

The choice of the optimum conductive admixture having, unlike NH_4Cl [7, 8], a sufficient stability and conductivity was made by testing various materials in two 'model' syntheses, in the preparation of $Ti(OEt)_4$ and $Zr(OPr-i)_4 \cdot i\text{-PrOH}$. The first product is easy to isolate by distillation, and the second one precipitates in the crystalline form after cooling the electrolyte to room temperature. Anodic metal dissolution and evolution of hydrogen at the cathode started at room temperature, the solution warmed up during the process which further proceeded in refluxing electrolyte.

The specific conductivities of the admixtures studied, $(Bu_4N)Br$, $(Et_4N)Cl$, $(Bu_4N)BF_4$, NaBr, NH_4Cl, NH_4Br, NH_4BF_4, $(R_4N)OPr-i$ in ethanol and isopropanol were of the same order of magnitude, 10^{-3} to 10^{-4} ohm^{-1} cm^{-1} at 20 °C and 10^{-2} to 10^{-3} ohm^{-1} cm^{-1} at 70 °C. The most suitable admixtures are $(Bu_4N)Br$, $(Bu_4N)BF_4$ and NaBr. With these substances, the process may be run for an indefinitely long period of time whereas with salts containing the NH_4^+ cation or Cl^- anion, the solution conductivity decreases and the process ceases after the transfer of 0.6 to 2.0 ampere-hours of electricity through the electrolyte.

Further syntheses were carried out with $(Bu_4N)Br$ as conductive admixture. The results obtained for yttrium, scandium, gallium and zirconium isopropoxides and titanium, germanium, niobium and tantalum ethoxides show that anodic dissolution of metals may be recommended as a technique for the synthesis of these compounds: the process goes smoothly and in sufficiently high current yields; with the most active metals, Sc and Y, the yields were nearly quantitative (Table I). The alkoxides isolated were characterized by elemental analyses and mass spectrometrically (the mass spectra agree well with the literature data [9]).

Attempts to extend the method described with the use of $(Bu_4N)Br$ to syntheses of beryllium, magnesium, zinc and aluminium ethoxides or isopropoxides proved a failure. The solid deposits formed contained variable amounts of bromine that could not be removed even by prolonged reflux in the alcohol. It seems likely that the products were polymeric metal oxo- or hydroxo alkoxohalides $M(OR)_n Hal_m X_p$ (X may be O, OH); the carbon percentages were significantly lower than the values calculated for $M(OR)_n$ or $MHal_n(OR)_m$. At high current densities and temperatures, anode deposits containing no

TABLE I. Electrochemical Synthesis of M(OR)$_n$ and Characteristics of Reaction Products.

Anode	ROH	Voltage (Volts)	Current (Amps)	Time, hrs	Product	Yield*		Form of products and isolation conditions	Analytical data Found (calcd.)			Degree of association of oligomers (mass spectrometric data)
						g	% current yield		% M	% C	% H	
Ga	i-PrOH	30	0.18	12	Ga(OPr-i)$_3$	4.2	64	Colourless liquid, b.p. 120–130 °C/1 mm	28.1 (28.3)	43.6 (43.7)	8.47 (8.50)	2
Sc	i-PrOH	30	0.18	12	Sc(OPr-i)$_3$	5.6	95	Needle crystals, isolated on cooling the solution	20.4 (20.3)	48.7 (48.6)	9.12 (9.45)	5, 4, 2
Y	i-PrOH	110	0.07	12	Y(OPr-i)$_3$	2.7	97	The same	33.2 (33.4)	40.9 (40.6)	8.17 (7.90)	4
Ge	EtOH	30	0.18	12	Ge(OEt)$_4$	3.6	72	Colourless liquid, b.p. 75°/10 mm	28.6 (28.8)	37.9 (37.9)	7.95 (7.90)	1
Ti	EtOH	30	0.15	15	Ti(OEt)$_4$	3.0	62	Light-yellow liquid, b.p. 120°/1 mm	20.9 (21.0)	41.5 (42.1)	8.90 (8.77)	2, 1
Ti	i-PrOH	30	0.15	16	Ti(OPr-i)$_4$	5.6	87	The same b.p. 50–60°/1 mm	16.8 (16.9)	50.8 (50.7)	9.70 (9.85)	1
Zr**	i-PrOH	110	0.23	15	Zr(OPr-i)$_4$	9.4	73	Needle crystals of solvate, isolated on cooling the solution	23.5 (23.5)	45.6 (46.4)	9.32 (9.28)	3, 1
Nb	EtOH	30	0.20	11	Nb(OEt)$_5$	4.5	85	Light-yellow liquid, b.p. 160°/0.1 mm	29.4 (29.2)	31.3 (31.4)	7.94 (7.86)	2
Ta	EtOH	30	0.20	10	Ta(OEt)$_5$	5.5	91	The same, b.p. 140°/0.1 mm	44.8 (44.6)	29.1 (29.6)	6.02 (6.16)	2

*Determined from the concentration of M^{n+} in solution; yields based on metal were not determined because of partial crumbling of anodes during electrolysis. **Cathode made of zirconium; Zr(OPr-i)$_4$·i-PrOH precipitates on cooling the solution formed in the electrolysis (the analytical data for that product are given).

carbon at all were formed in the anodic oxidation of aluminium and lead.

With copper, lead, antimony and bismuth anodes, the initial electrolysis step (0.5 to 1 hr) went with hydrogen evolution at the platinum cathode and precipitation of $M(OR)_nHal_m$ in the anode space. The reactions then ceased and cathodic deposition of the metal (refining) occurred.

A brief discussion of possible mechanisms of the metal alkoxide formation in the anodic dissolution of metals in alcohol solutions of admixtures is needed to rationalize the results obtained.

According to Lehmkuhl [4], the formation of metal alkoxides at the cathode is the result of reduction of $MHal_n$, the first formed products of anodic oxidation of metals.
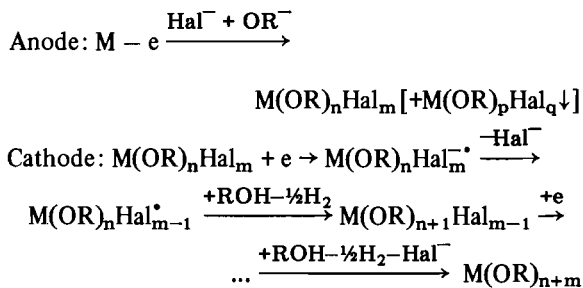
The results of this work, however, suggest that metals are transferred to the cathode space in the form of their alkoxoderivatives, $M(OR)_nHal_m$, rather than as symmetrical metal halides. We repeated the synthesis of $Ni(OEt)_2$ described in [4] in a glass cell with ceramic filter between anode and cathode spaces used specially for this experiment in order to detect intermediates. The initial products of anodic electrolysis were white and then yellowish-green precipitates. The colour change of the precipitate during the electrolysis was extremely rapid. The analysis of this deposit showed that this precipitate was not an individual substance; the ratio of the OR group over Br was about 1.1:1 at the first moment and about 1.9 to 1 afterwards. So, probably this precipitate is comprised of various nickel ethoxo- bromides (*e.g.* $Ni(OR)BrNi_3(OR)_4Br_2$ [10]).

Crystallization of violet $Ni(OEt)_2$ at the cathode only begins after accumulation of OR groups in a certain concentration according to the analytical data, 1 Ni atom and $\geqslant 2$ OR groups are present per 3 $(R_4N)Br$ in solution (the maximal concentration of $(Bu_4N)Br$ at that moment amounts of 0.06 N). With Cu, Pb, Sb, Bi as anode materials the cathodic reaction (leading in that case to reduction to metals) started only after the formation of insoluble metal alkoxohalide deposits at the anodes and attainment of certain metal ion and OR concentrations in the solution which also contained $(R_4N)Br$.

With soluble metal alkoxohalides, a decrease of solution conductivity at the first stage of the process is indicative of binding Hal^- to $M(OR)_nHal_m$ and $(R'_4N)^+$ to $(R'_4N)OR$. The formation of $M(OR)_n$-Hal_m in solutions as intermediates seems to be probable enough, the more so that these products have high thermodynamic stabilities (as is known $M(OR)_n$ reacts with $MHal_n$ with considerable energy release). The transfer of non-dissociated molecules $M(OR)_nHal_m$ to the cathode may be a more mechanical process.

The cathodic reduction of $M(OR)_nHal_m$ may involve the formation of an anion-radical, elimination
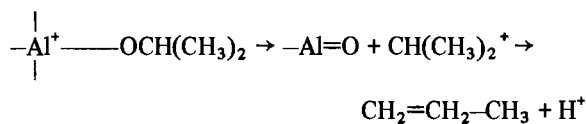
of the halide anion, and subsequent interaction of the radical formed with alcohol accompanied by hydrogen evolution:

$$Anode: M - e \xrightarrow{\;Hal^- + OR^-\;}$$

$$M(OR)_nHal_m\,[+M(OR)_pHal_q{\downarrow}]$$

$$Cathode: M(OR)_nHal_m + e \rightarrow M(OR)_nHal_m^{-\bullet} \xrightarrow{\;-Hal^-\;}$$

$$M(OR)_nHal_{m-1}^{\bullet} \xrightarrow{\;+ROH-\frac{1}{2}H_2\;} M(OR)_{n+1}Hal_{m-1} \xrightarrow{\;+e\;}$$

$$\ldots \xrightarrow{\;+ROH-\frac{1}{2}H_2-Hal^-\;} M(OR)_{n+m}$$

With $M(OR)_pHal_q$ having low solubilities which cannot be transferred to the cathode, the process terminates at the step of the formation of a metal alkoxohalide. The accumulation of a soluble metal alkoxide affects the composition of the dominant $M(OR)_p$-Hal_q species in solution (p increases and q decreases). This is accompanied by the increase of metal alkoxohalide reduction potential to that of cathode-inactive metal alkoxide. As reduction potentials of metal bromides (and iodides) in organic solvents are lower than those of metal chlorides (for $TiHal_4$, ΔE is equal to *ca.* 0.5 v [11]) reaction terminates with the accumulation of $M(OR)_pHal_q$ in solution only if a chlorine containing admixture is used. In the synthesis of $Ti(OEt)_4$, the Ti:Cl ratio at the moment of reaction termination is equal to (7 to 10):1, that is the reduction of $Ti(OEt)_{4-n}Cl_n$ proceeds if only n $<$ 0.1–0.2.

In the electrolysis with anodes made of Cu, Pb, Sb and Bi, even metal alkoxobromide reduction potentials prove to be higher than the potentials of pure metal deposition are.

The formation of oxo- or hydroxo-complexes at anodes made of Al, Be, Mg *etc.* may be due to spontaneous reactions of these metals with alcohols. This must lead to an increase in anode potential and hence to dehydration of alcohols, particularly alcohols of the iso-structure. For instance:

$$-\overset{\displaystyle |}{\underset{\displaystyle |}{Al}}{}^+\!\!-\!\!-\!\!-OCH(CH_3)_2 \rightarrow -Al{=}O + CH(CH_3)_2{}^+ \rightarrow$$

$$CH_2{=}CH_2{-}CH_3 + H^+$$

Decrease of current density hinders these side processes to some degree. Thus, Sc and Y alkoxides are formed in high yields only if porous metals are used as anode materials. With solid anodes having polished surfaces the process is complicated by the formation of olefinic hydrocarbons.

The direct electrochemical synthesis of metal alkoxides may thus be recommended only for metals having normal hydrogen potentials in the range 0.1 to 2 v and forming alkoxohalide intermediates soluble in the electrolyte. The potential necessary for the

reduction of $M(OR)_n Hal_m$ is attained under normal conditions and proves to be lower than the potential of metal deposition (refining).

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