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Single-Crystal Synthesis of Low-Valency Molybdenum Compounds by Slow Cooling of Electrolyzed Li_2MoO_4–MoO_3 Melts

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Li_2MoO_4–MoO_3 melts in Al_2O_3 crucibles were electrolyzed at 650°C and then slowly cooled to obtain crystals of the reduced molybdates formed. Crystallization occurred throughout the melt and not on the electrodes. In addition to MoO_2 and the known bronze $Li_{0.33}MoO_3$, single crystals of three new compounds have been identified: (1) $Li_2Al_2Mo_4O_{15}$ triclinic; $a = 6.636 \pm 0.002$ Å, $b = 7.158 \pm 0.002$ Å, $c = 7.055 \pm 0.002$ Å, $\alpha = 90.95 \pm 0.03°$, $\beta = 105.32 \pm 0.03°$, $\gamma = 110.9 \pm 0.03°$; (2) $Li_{1.3}Mo_3O_8$, triclinic; $a = 8.256 \pm 0.006$ Å, $b = 8.550 \pm 0.007$ Å, $c = 11.36 \pm 0.01$ Å, $\alpha = 96.7 \pm 0.1°$, $\beta = 70.5 \pm 0.1°$, $\gamma = 87.5 \pm 0.1°$; (3) $Li_{0.1}Mo_4O_7$, orthorhombic, space group *Pbnb*, $a = 7.475 \pm 0.007$ Å, $b = 24.94 \pm 0.07$ Å, $c = 29.4 \pm 0.1$ Å. The formation of these compounds depends on the composition of the melt and the duration of electrolysis. There is some evidence that these compounds are not products of electrode reactions but are formed by secondary reactions in the melt between the primary products of electrolysis.

Introduction

Crystals of several molybdenum bronzes have been prepared by electrolysis of molybdate melts (*1–6*). In these studies the crystals were grown on the cathode. It is reasonable to assume that some of the reduced phases might remain in the melt without crystallizing on the electrode. The aim of this study was to investigate conditions for the growth of crystals of such reduced phases formed during the electrolysis of Li_2MoO_4–MoO_3 mixtures by cooling the electrolyzed melts slowly. Crystals of new oxides of molybdenum have been obtained in this manner and the results are reported in this paper.

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Experimental

Li_2MoO_4–MoO_3 (Alfa 98.5% purity and Baker analyzed, respectively) mixtures in various ratios were melted in high-purity Al_2O_3 (McDanel) crucibles at 650°C and electrolyzed in a flowing N_2 atmosphere at a voltage of 0.5–1.0 V and current density of 6–8 mA/cm^2 for 7–10 days. (Details of the method have been described earlier (*4*).) Subsequently, the melt was cooled at 10°C/hr while the passage of current continued until it dropped to zero due to solidification of the melt. The contents of the crucibles were leached with boiling water after which the crystals could be separated mechanically. Most of the melt was found to have crystallized, with several different phases being present. The stoichiometries of

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the phases were identified by elemental analysis of Li, Al, and Mo measured by a microprocessor controlled Beckman-Spectrametrics Spectra Span III B DCT Basic Multi dc-Argon plasma emission spectrometer. Single-crystal X-ray diffraction Weissenberg and precession methods (with Zr-filtered molybdenum radiation) were used to determine the crystallographic properties. Powder X-ray diffraction patterns of crushed crystals were obtained with a Norelco diffractometer using nickel-filtered copper radiation.

Results

The results of several electrolysis experiments using various Li_2MoO_4–MoO_3 starting composition are summarized in Table I.

Three new molybdenum oxides were found to form in the melt: (1) Transparent dark-blue crystals of $Li_{1.3}Mo_3O_8$ which are

TABLE I

RESULTS OF ELECTROLYSIS CRYSTAL GROWTH

No.	Melt $MoO_3 : Li_2MoO_4$	Current start → end (mA)	Voltage start → end (V)	Duration (Days)	Crystals obtained
1	0.5	6 → 8	0.5 → 0.2	7	MoO_2 crystals
2	1.0	6 → 8	0.5 → 0.2	7	MoO_2 crystals
3	1.5	6.5 → 6.0	0.5 → 0.7	4	Transparent orange–red crystals ($Li_2Al_2Mo_4O_{15}$) bulky, 10 × 3 × 2 mm. Transparent blue crystals ($Li_{1.3}Mo_3O_8$) rod-shaped 5 × 3 × 3 mm
4	1.5	6.5 → 6.0	0.5 → 0.7	14	Same result as No. 3
5	1.75	6.5 → 6.0	0.5 → 0.7	4	$Li_2Al_2Mo_4O_{15}$, $Li_{1.3}Mo_3O_8$ crystals and violet–blue bronze needles (Li_xMoO_3)
6	2.3	6.5 → 6.0	0.5 → 0.7	4	$Li_{1.3}Mo_3O_8$, $Li_2Al_2Mo_4O_{15}$, and Li_xMoO_3 bronze crystals
7	2.3	80	3.5	7	Much of the melt is converted to violet–blue bronze (Li_xMoO_3) and MoO_2 crystals. $Li_2Al_2Mo_4O_{15}$ crystals are present, but the blue $Li_{1.3}Mo_3O_8$ phase is absent
8	2.5	6.5 → 6.0	0.5 → 0.7	2	No Li_xMoO_3 bronze, only blue $Li_{1.3}Mo_3O_8$ and orange–red $Li_2Al_2Mo_4O_{15}$ crystals
9	2.5	6 → 6.5	0.5 → 0.7	7	Large amount of Li_xMoO_3 bronze crystals throughout the melt; ill-shaped crystalline agglomerates 5 × 3 × 3 mm, which cleave easily into thin platelets
10	3.5	6 → 6.5	0.5 → 0.7	10	Bronze crystals (Li_xMoO_3) and dark-blue oriented polycrystalline agglomerates ($Li_{0.1}Mo_4O_7$), which can be cleaved into small single crystals 1 × 0.2 × 0.2 mm
11	5	40	4	4	MoO_3, MoO_2 crystals, and dark-blue polycrystals of $Li_{0.1}Mo_4O_7$
12	6.5	6 → 6.5	0.5 → 0.7	7	Same as No. 11

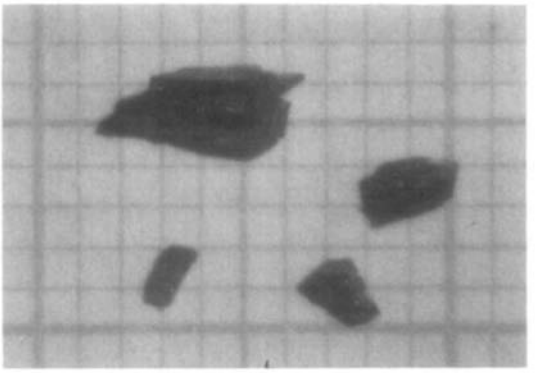

FIG. 1. Crystals of $Li_{1.3}Mo_3O_8$.

triclinic with $a = 8.256 \pm 0.006$ Å, $b = 8.550 \pm 0.007$ Å, $c = 11.36 \pm 0.01$ Å, $\alpha = 96.7 \pm 0.1°$, $\beta = 70.5 \pm 0.1°$, $\gamma = 87.5 \pm 0.1°$; (2) transparent orange–red triclinic crystals of $Li_2Al_2Mo_4O_{15}$ with lattice parameters $a = 6.636 \pm 0.002$ Å, $b = 7.158 \pm 0.002$ Å, $c = 7.055 \pm 0.002$ Å, $\alpha = 90.95 \pm 0.03°$, $\beta = 105.32 \pm 0.03°$, $\gamma = 110.9 \pm 0.03°$; (3) dark-blue opaque crystals of $Li_{0.1}Mo_4O_7$ which are orthorhombic with space group *Pbnb* (No. 56) and $a = 7.475 \pm 0.007$ Å, $b = 24.94 \pm 0.07$ Å, and $c = 29.4 \pm 0.1$ Å.

Figures 1, 2, and 3 show representative crystals of $Li_{1.3}Mo_3O_8$, $Li_2Al_2Mo_2O_{15}$, and $Li_{0.1}Mo_4O_7$, respectively.

The X-ray powder diffraction patterns of these compounds are given in Tables II, III,

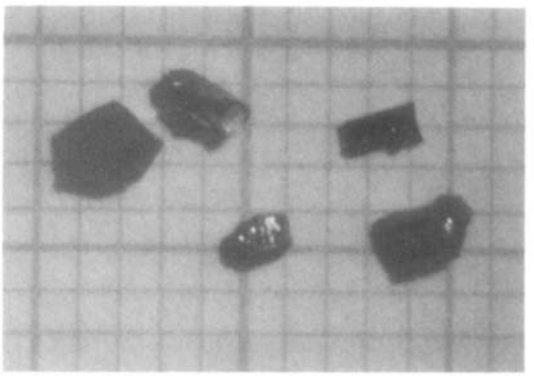

FIG. 2. Crystals of $Li_2Al_2Mo_4O_{15}$.

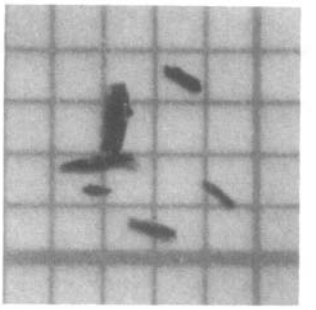

FIG. 3. Crystals of $Li_{0.1}Mo_4O_7$.

and IV. A computer program was used to index the powder patterns based on the lattice parameters determined by the single crystal studies.

Results of the chemical analysis are given in Table V.

The transparent crystals, $Li_{1.3}Mo_3O_8$ and $Li_2Al_2Mo_4O_{15}$, are insulators ($\rho > 10^6\ \Omega$ cm) the dark-blue crystals, $Li_{0.1}Mo_4O_7$, are elec-

TABLE II

X-RAY POWDER DIFFRACTION PATTERN OF $Li_{1.3}Mo_3O_8$

d_{obs} (Å)	d_{cal} (Å)	I_{rel}	*hkl*
7.16	7.11	30	$0\bar{1}1$
6.21	6.20	5	011
5.35	5.30	90	002, 102
4.23	4.23	10	012, 020
4.13	4.12	5	$1\bar{2}1$, 201
3.84	3.83	15	120, $\bar{1}02$
3.74	3.74	5	021, 103
3.62	3.65	10	210
3.56	3.57	100	$12\bar{1}$, $0\bar{2}2$, $1\bar{1}3$
3.10	3.10	30	$0\bar{2}2$
2.823	2.822	30	$0\bar{3}1$, 104, 303
2.702	2.695	10	$21\bar{2}$
2.672	2.664	15	123
2.553	2.553	20	$12\bar{3}$
2.447	2.441	10	$3\bar{1}3$, $13\bar{2}$, $22\bar{2}$
2.209	2.204	10	205
2.138	2.143	45	133, $12\bar{4}$
2.128	2.129	20	$0\bar{1}5$, $\bar{1}14$
2.033	2.033	10	$2\bar{2}5$, 401
1.869	1.864	10	$4\bar{1}4$
1.687	1.687	10	$3\bar{3}5$, $13\bar{5}$, 342

TABLE III

X-RAY POWDER DIFFRACTION PATTERN OF $Li_{0.1}Mo_4O_7$

d_{obs} (Å)	d_{cal} (Å)	I_{rel}	*hkl*
6.65	6.66	5	102
4.43	4.43	20	134
4.04	4.04	100	135
3.96	3.99	10	152
3.46	3.46	25	072; 213
3.42	3.41	25	230
2.996	2.991	10	250
2.829	2.823	5 broad	182; 175
2.674	2.673	10	263
2.604	2.599	10	264; 190
2.024	2.022	25	372
1.937	1.938	10 broad	2,11,0
1.865	1.864	10	401; 410

trically conducting, as determined by two-probe conductivity measurements. The crystals of $Li_{0.1}Mo_4O_7$ are too small for meaningful four-probe conductivity measurements.

In addition to the new compounds described above, crystals of the violet–blue bronze $Li_{0.3}MoO_3$ (reported by Strobel and Greenblatt (*4*)) and MoO_2 are also formed. In all of the experiments a dark-blue sublimate was formed on the upper parts of the reaction tube. Its X-ray powder pattern showed only a few weak, broad lines, indicative of poor crystallinity. The sublimate was always contaminated with small amounts of MoO_3 and therefore, characterization by chemical analysis was not attempted.

TABLE IV

X-RAY POWDER DIFFRACTION OF $Li_2Al_2Mo_4O_{15}$

d_{obs} (Å)	d_{cal} (Å)	I_{rel}	*khl*
6.65	6.64	25	010
5.94	5.93	15	100
5.58	5.58	15	$1\bar{1}0$
5.27	5.27	15	$10\bar{1}$
4.72	4.71	80	$\bar{1}11$
4.48	4.47	15	011
4.00	3.99	90	$1\bar{1}1$
3.78	3.78	15	110
3.73	3.72	80	$11\bar{1}$
3.52	3.51	70	$1\bar{2}0$
3.38	3.38	100	$10\bar{2}$
3.33	3.32	80	$02\bar{0}$
3.20	3.21	70	$2\bar{1}\bar{1}$
3.13	3.13	80	$02\bar{1}$, $\bar{1}12$
3.07	3.06	15	$\bar{1}21$, $20\bar{1}$
2.990	2.988	60	111
2.968	2.967	50	200
2.864	2.870	VW	012
2.794	2.791	10	$2\bar{2}0$
2.642	2.639	15	$2\bar{1}1$, $20\bar{2}$
2.521	2.522	70	$\bar{1}20$
2.486	2.485	80	$21\bar{1}$, $\bar{1}22$
2.396	2.395	15	210
2.259	2.261	15	$1\bar{3}1$
2.072	2.072	70	$2\bar{1}2$
1.886	1.887	15	220, $13\bar{1}$, $3\bar{1}1$
1.861	1.861	50	$22\bar{2}$, $3\bar{3}0$, $1\bar{2}3$
1.760	1.760	40	$\bar{3}32$, $30\bar{3}$

Discussion

The formation of various compounds in the electrolyzed melts (at 650°C) depends on the MoO_3 content of the melt. When the $MoO_3 : Li_2MoO_4$ ratio is <1 the major product is MoO_2 grown on the cathode. As the

TABLE V

RESULTS OF CHEMICAL ANALYSIS

No.	Sample	%Li (obs)	%Mo (obs)	%Al (obs)	Calcd. formula
3	Orange–red crystals	1.90	55.19	7.80	$Li_2Al_{1.93}Mo_{4.12}O_{14.6}$
5	Orange–red crystals	1.90	56.68	8.02	$Li_2Al_{2.17}Mo_{4.20}O_{15.2}$
5	Transparent blue crystals	2.07	68.22	0.0	$Li_{1.3}Mo_3O_8$
10	Opaque dark-blue crystals	0.15	79.93	0.0	$Li_{0.1}Mo_4O_{7.4}$

MoO_3 content is increased the transparent orange–red crystals of $Li_2Al_2Mo_4O_{15}$ (aluminum is incorporated due to attack of the alumina crucible by the melt) are also formed. The color of these crystals changed from light orange–red to reddish-brown when either the MoO_3 content increased or the duration of the electrolysis was lengthened. However, chemical analysis of the darker phases did not show a significant change of stoichiometry from $Li_2Al_2Mo_4O_{15}$ and the X-ray powder patterns of the differently colored phases were identical. A new transparent dark-blue phase, $Li_{1.3}Mo_3O_8$ and the known bronze (4) $Li_{0.3}MoO_3$, appears when more than 1.5 mole of MoO_3 per mole of Li_2MoO_4 is present. Increasing the $MoO_3 : Li_2MoO_4$ ratio to 3.5 yields a new bronze-looking dark-blue phase $Li_{0.1}Mo_4O_7$ along with $Li_{0.3}MoO_3$. When $MoO_3 : Li_2MoO_4 = 6.5$ $Li_{0.1}Mo_4O_7$ and MoO_2 crystals are obtained. The red ($Li_2Al_2Mo_4O_{15}$) and blue ($Li_{1.3}Mo_3O_8$) oxides were not found in the melt.

It should be emphasized that only MoO_2 crystals were found to have grown on the cathode. All other crystals formed throughout the melt. MoO_2 crystals were also found throughout the melt in those cases when the $MoO_3 : Li_2MoO_4$ content was greater than one. However, the morphology of the MoO_2 crystals grown in the melt and on the cathode are significantly different as shown in Figs. 4a,b. An interesting feature of the cathode grown samples is the intergrowths of crystals (Fig. 4a) at an angle corresponding to the monoclinic unique angle ($\beta = 119.37°$) in MoO_2. The bronze $Li_{0.3}MoO_3$ always appeared with the $Li_{1.3}Mo_3O_8$ phase. Crystals of $Li_{1.3}Mo_3O_8$ were found to form in association with MoO_3 crystals.

More MoO_3 in the melt seems to favor more reduced compounds. Thus more of the orange–red $Li_2Al_2Mo_4O_{15}$ (with an average molybdenum valency of 5.5) is formed in a Li_2MoO_4-rich melt. As the MoO_3 content increases the blue $Li_{1.3}Mo_3O_8$ with an average Mo valency of 4.9 (at 60% mole MoO_3) and $Li_{0.1}Mo_4O_7$ with an average Mo valency of 3.475 (at 78% mole MoO_3) appear. At 87% mole MoO_3 only MoO_2 and $Li_{0.1}Mo_4O_7$ are present. $Li_2Al_2Mo_4O_{15}$, $Li_{1.3}Mo_3O_8$, and $Li_{0.33}MoO_3$ are not formed.

We find under the conditions of this experiment that the $Li_{0.3}MoO_3$ bronze is stable at 650°C in contrast to Reau *et al.* (*7*) who reported that when $Li_{0.33}MoO_3$ was heated to 590°C it decomposed to MoO_2 and Mo_4O_{11} in their solid-state reactions. This could imply that in our experiment there is an equilibrium between the melt and solid $Li_{0.3}MoO_3$ which may result in its stability at the higher temperature.

In previous electrolysis experiments carried out at 560°C we reported that the growth of violet–blue $Li_{0.3}MoO_3$ crystals occurred in a limited range of melt composition (*4*). At 650°C these bronze crystals formed from a wide range of $MoO_3 : Li_2MoO_4$ melt mixtures (1.75–3.5).

The color and morphology of the $Li_{0.3}MoO_3$ crystals formed in this work at 650°C in the melt are similar to the crystals found on the cathode at 560°C (*4*). However, the X-ray diffraction powder patterns show a small but significant shift to lower values of *d* spacings relative to the Li_xMoO_3 samples obtained from the melt at 650°C. Chemical analysis of the violet–blue bronze phase (650°C from the melt) indicates $Li_{0.3}MoO_3$ stoichiometry.

$Li_{0.3}MoO_3$ bronze crystals were obtained only when the electrolysis was carried out for a sufficiently long time (Table I). For example, in a $MoO_3 : Li_2MoO_4 = 2.5$ melt composition electrolysis for 2 days produced only $Li_2Al_2Mo_4O_{15}$, $Li_{1.3}Mo_3O_8$, and the unidentified blue sublimate. However, continued electrolysis for 7 days produced the bronze $Li_{0.3}MoO_3$ and MoO_2. This might indicate that reactions in the melt proceed by several steps and the bronze is

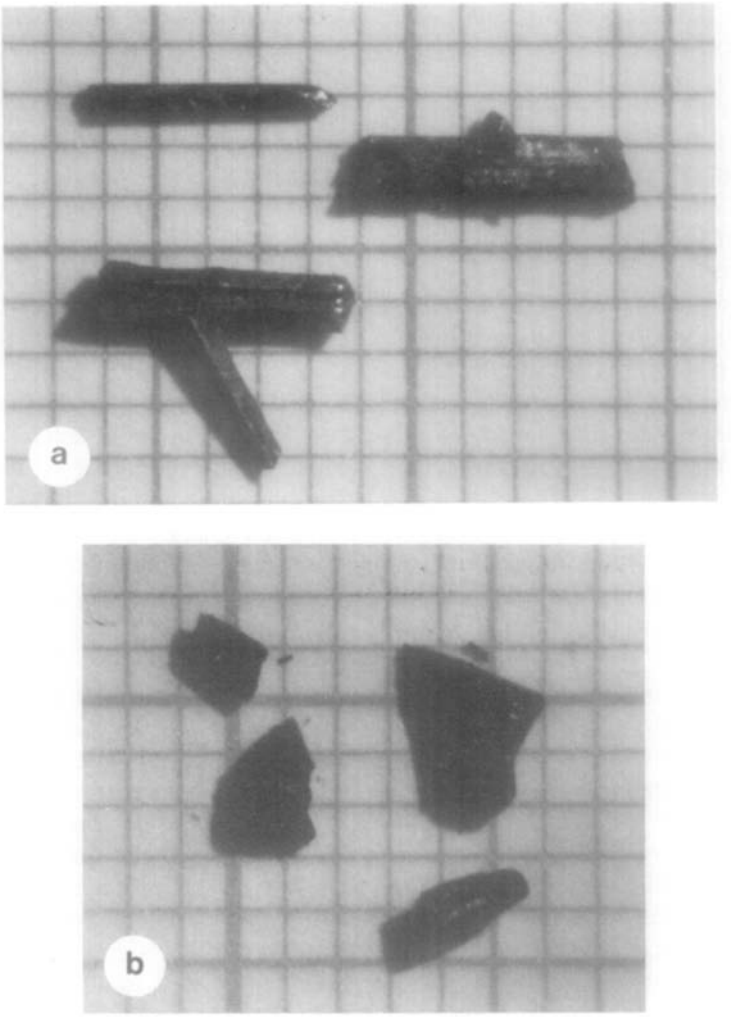

FIG. 4. (a) Crystals of MoO_2 grown on the cathode. (b) Crystals of MoO_2 grown throughout the melt.

formed by a secondary reaction between primary products of electrolysis.

The unidentified blue sublimate formed in our experiments was probably produced by cathodic reduction. (It was also present when pure Li_2MoO_4 was electrolyzed at 750°C). We have reacted this blue sublimate with the orange–red compound ($Li_2Al_2Mo_4O_{15}$) in evacuated quartz ampoules at 650°C for 1 week and obtained MoO_2. Reaction of the blue sublimate with MoO_3 under similar conditions yielded Mo_4O_{11}. An analogous reaction of the blue sublimate with $Li_{1.3}Mo_3O_8$ produced the bronze $Li_{0.3}MoO_3$. This suggests that the blue sublimate might contain a slightly reduced molybdenum oxide species corresponding to MoO_{3-x} and the reaction

$$Li_{1.3}Mo_3O_8 + MoO_{3-x} \xrightarrow[650°C]{\text{vac}} Li_{1.3}Mo_4O_{11-x}$$

took place. This compound corresponds closely to the stoichiometry we found for $Li_{0.3}MoO_3$.

These experimental observations support our hypothesis that the compounds obtained are formed by secondary reactions between primary products of electrolysis.

Similar secondary reactions have been reported in an earlier work on the electrolysis of MoO_3 in LiCl–KCl flux (*8*) at 450°C, MoO_2Cl_2 and $Li_2Mo_2O_7$ (formed in the melt by chemical reaction, before electrolysis) were reduced electrochemically to MoO_2. A second reduced product $Li_5Mo_2O_8$ found on the cathode was attributed to the reduction of MoO_4^{2-} which formed as a secondary reaction product in the primary reduction step.

The transparent orange–red $Li_2Al_2Mo_4O_{15}$ and dark-blue $Li_{1.3}Mo_3O_8$ crystals with an average molybdenum oxydation state of 5.5 and 4.9, respectively, probably contain reduced molybdenum ions with localized electrons. The dark-blue $Li_{0.1}Mo_4O_7$ crystals with a bronze sheen have an average molybdenum valence of 3.475. With the exception of the $LiMoO_2$ insertion compound (*9*), all other molybdenum oxides whose structures have been determined earlier have been found to contain molybdenum clusters if the oxidation state of Mo is less than 4 (*10*). We plan to investigate the structural properties of these new phases in more detail.

Conclusion

Single crystals of three new reduced molybdates were synthesized by slow cooling of electrolyzed Li_2MoO_4:MoO_3 melts at 650°C: $Li_2Al_2Mo_4O_{15}$, $Li_{1.3}Mo_3O_8$, and $Li_{0.1}Mo_4O_7$. In addition MoO_2 and the known bronze $Li_{0.3}MoO_3$ crystals have also been obtained. Crystallization occurred throughout the melt and not on the electrodes. There is evidence that some of these compounds are the result of secondary reactions in the melt between the primary products of electrolysis.

Acknowledgments

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