Electrode and Redox Potentials of Molybdenum and Stability of Molybdenum Chloro-Species in Alkali Chloride Melts

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Molybdenum electrode and Mo(III)/(IV) redox potentials were measured in fused alkali chlorides. Experiments were performed in individual salts (LiCl, NaCl, KCl, RbCl and CsCl) and in several binary and ternary eutectic or low-melting mixtures between 633 and 1173 K (depending on the melting point of the solvent salt). Formal standard electrode potentials $E^{\circ}_{\text{Mo}/\text{Mo(III)}}$ and redox potentials $E^{\circ}_{\text{Mo(III)}/\text{Mo(IV)}}$ in respect to Cl^-/Cl_2 couple and Gibbs free energy change of formation of molybdenum(III) chloride in alkali chloride melts were calculated. Electronic absorption spectra of Mo(III) ions were recorded, and spectroscopic parameters of MoCl_6^{3-} complex ions determined. High temperature spectroscopy measurements were used to study the stability of Mo(III) chloro-species in fused chlorides and the reaction rates of Mo(III) ions disproportionation were also determined. Diffusion coefficients of molybdenum ions in LiCl-KCl-CsCl and NaCl-CsCl eutectic based melts were determined from the results of electrochemical measurements.

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Molybdenum has many properties (including high melting point, corrosion resistance, and good strength at elevated temperatures, low thermal neutron capture cross-section, good thermal conductivity and a relatively low thermal expansion coefficient) that make it attractive for various industrial applications. Molybdenum is also of great interest for the nuclear energy field as a construction and a nuclear fuel component material. Of all types of uranium nuclear fuels, metallic uranium obviously offers the highest concentration of the fissile material. Depending on temperature, pure solid uranium can exist in one of three phases (α , β or γ) and the temperature of $\beta \rightarrow \gamma$ transformation is 1049 K. The high temperature γ -U phase exhibits the best performance under irradiation.^{1,2} To stabilize this phase at room temperature a number of alloying elements can be employed (e.g., Nb, Zr, Mo, etc.), of which molybdenum attracted the most attention on the basis of its cost and the required concentration in the alloy.^{2–4}

Molten salts can be employed in a number of technological processes involving molybdenum. Alkali chloride based melts can serve as electrolytes for molybdenum electrowinning and electrorefining, as well as for producing molybdenum coatings on other metals. Pyrochemical reprocessing of spent nuclear fuels (SNFs) is another field where molten salts can be employed, and this is a feasible option for treating irradiated U-Mo based metallic fuels. Non-aqueous high-temperature pyrochemical reprocessing can also be used for other types SNFs, where molybdenum has accumulated as a fission product. In metallic SNFs molybdenum is present in the elemental form, whereas in the oxide fuels this element forms molybdate(VI) species, Mo(IV) oxide (with very limited solubility in the UO_2 matrix) and molybdenum metal (alloyed with Tc, Ru, Rh and Pd).^{5–7} Designing a molten salt electrochemical process relies on information concerning molybdenum speciation, properties and its behavior in the electrolyte.

Some aspects of molybdenum chemistry in fused chlorides were considered earlier,⁸ primarily in relation to pyrochemical reprocessing, but these did not include electrochemical processes. Electrochemistry of molybdenum in chloride melts first attracted attention several decades ago but no systematic study of the electrode potentials has been performed, with the exception of the earlier studies by Ryzhik and Smirnov.^{9–16} They determined molybdenum standard electrode

potentials in melts based on individual alkali chlorides (LiCl, KCl, CsCl) and in the LiCl-KCl eutectic mixture. Their results, however, did not agree with the data by Senderoff and Brenner¹⁷ and Selis,¹⁸ who reported significantly more positive potential values for LiCl-KCl based melts at 873–1173 K and 733–813 K, respectively. Subsequent measurements in NaCl-KCl equimolar mixture at 992–1088 K^{19,20} and NaCl-CsCl eutectic at 845–1010 K²¹ also resulted in more positive molybdenum electrode potential values than could have been expected from the data of Ryzhik and Smirnov. Thus, there was noticeable disagreement between the data reported over the past years. Very little attention was subsequently paid to measuring molybdenum electrode potentials in fused chlorides.

Molybdenum is a polyvalent metal and it is generally agreed now that the lowest oxidation state of molybdenum in high temperature chloride melts is +3.^{17–21} Such observation corresponds to the trend of increasing the lowest stable oxidation state of transition *d*-block metal ions in chloride melts upon increasing the period number, i.e. from 3*d* to 4*d* and 5*d*. For instance, the lowest oxidation state of chromium in chloride melts is +2²² and that of tungsten is +4.^{23,24} Co-deposition of lower oxidation state molybdenum species together with the metal on a cathode was observed during electrolysis at low temperatures (in NaCl-KCl-CsCl and NaCl-KCl-MgCl₂ based melts) at high molybdenum concentrations.²⁵ This compound was not characterized and was said to be insoluble in the melt. Earlier reports also mentioned a possibility that polynuclear molybdenum(III) ions can exist in the melts^{26–28} but subsequent spectroscopy studies produced no evidence of such species. Higher oxidation states of molybdenum in fused chlorides have yet to be sufficiently studied. Molybdenum(IV) and (V) chloro-species could be formed under certain conditions and were characterised primarily by spectroscopy.^{29–31} Molybdenum(VI) species can be present in chloride melts only in the form of oxygen containing ions.

The present study was aimed at studying molybdenum electrochemical properties and speciation in alkali chloride based melts, focusing on molybdenum electrode potentials and probing the Mo(III)/Mo(IV) oxidation-reduction process.

Experimental

To assess the effect of the melt cationic composition on molybdenum speciation and behavior, the experiments were performed in

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individual alkali chlorides (LiCl, NaCl, KCl, RbCl, CsCl), as well as in several binary and ternary mixtures of eutectic or low melting compositions. These included LiCl-KCl (58 mol.% KCl, m.p. 625 K); NaCl-KCl (50 mol.% NaCl, m.p. 923 K); NaCl-CsCl (34 mol.% NaCl, m.p. 763 K), KCl-CsCl (36 mol.% KCl, m.p. 879 K); LiCl-KCl-CsCl (57.5 mol.% LiCl, 16.5 mol.% KCl, m.p. 536 K) and NaCl-KCl-CsCl (30 mol.% NaCl, 24.5 mol.% KCl, m.p. 753 K) mixtures. Commercially available alkali chlorides were used and these included LiCl (99+ %, Aldrich), NaCl (99.9+ %, Reakhim), KCl (99.8+ %, Reakhim) and CsCl (99.9+ %, Reakhim). Salts were dried under vacuum at 573 K for 3 hours in silica cells. The temperature was then increased to ca. 50 degrees above the melting point of the salt. The cell was filled with argon (99.998%) and the molten salt was sparged with gaseous hydrogen chloride or a mixture of chlorine and hydrogen chloride for several hours and then held under vacuum to remove the gases dissolved. Mixtures of alkali chlorides were prepared by fusing together the individual salts thus prepared. All salt mixtures were stored in an argon filled dry box prior to use.

Molybdenum-containing melts were produced either by anodic dissolution of the metal or by dissolving potassium hexachloromolybdate(III). The latter compound was prepared using the procedure given by Senderoff and Brenner;³² starting potassium molybdate was synthesized by reacting stoichiometric amounts of molybdenum trioxide (99.5+ %, Reakhim) and potassium carbonate (99+ %, Reakhim). The impurities content in the compound prepared was not determined. Molybdenum metal (99.95%, wire and foil) was obtained from Alfa Aesar. Anodic dissolution of molybdenum is a three-electron process.^{33,34} Previous high temperature spectroscopy studies showed that six-coordinated MoCl_6^{3-} ions were formed in the melt irrespectively of the method used for introducing molybdenum ions (anodic dissolution of the metal or dissolution of K_3MoCl_6).^{31,35} The concentration of molybdenum in the quenched melt samples was determined photometrically with thiocyanate.³⁶ Volumetric analysis (oxidimetric titration) was employed to estimate the mean oxidation state of molybdenum in the quenched melts.³⁷ A sample of the melt was dissolved in a known volume of ammonium vanadate solution (0.01 M in 5 M sulfuric acid) resulting in oxidation of all molybdenum to the oxidation state +6. The excess vanadate was then determined by titrating with Mohr salt solution (0.01 M of ammonium iron sulfate in 5 M H_2SO_4) in the presence of phenylanthranilic acid as redox indicator. The mean oxidation state of molybdenum (n_{ox}) was calculated using the following equation:

$$n_{ox} = 6 - (C_V \cdot V_V - C_{Fe} \cdot V_{Fe}) \cdot 95.94 / (m \cdot \omega_{Mo}), \quad [1]$$

where C_V and C_{Fe} are the concentrations of ammonium vanadate and Mohr salt solutions, respectively, M; V_V and V_{Fe} are the volumes of ammonium vanadate and Mohr salt solutions used, dm^3 ; m is the melt sample weight used for the analysis, g; and ω_{Mo} is molybdenum concentration in the melt, mass fraction.

High temperature spectroscopy measurements.—Electronic absorption spectra of molybdenum-containing melts were recorded between 350 and 1100 nm using a custom-built set-up based on a double channel spectrometer AvaSpec-2048FT-2-SPU (Avantes) and an optical furnace TF1726 (Instron SFL). The melts were held in standard 1 cm path length silica optical cells equipped with the necessary arrangements and electrodes, i.e., for performing molybdenum metal anodic dissolution, sampling the melt, etc. The electrodes were positioned in the cell that spectra could be recorded in the course of the metal anodic dissolution without interrupting the process.

Electrochemistry measurements.—Electrode potentials of molybdenum were determined using the electromotive force (emf) measurements method.^{10,38} Measurements were performed at zero current using an Autolab PGSTAT 302N potentiostat/galvanostat. Molybdenum plate (ca. 4 cm^2) attached to a molybdenum rod served as a working electrode. Chlorine (Cl^-/Cl_2) or silver chloride (Ag/AgCl) electrodes were used as references, and all the measured potentials were recalculated to Cl^-/Cl_2 couple. The chlorine reference

electrode was used in a number of experiments for verification of the values obtained with the silver chloride electrode. The chlorine electrode¹⁰ consisted of a silica sheath of ca 15 mm i.d. having an asbestos diaphragm (ca. 2 mm i.d.) in the bottom and containing the corresponding alkali chloride solvent melt. A graphite tube was dipped into the melt and a constant flow of gaseous chlorine was passed through this tube. The melt was thus kept saturated with chlorine and the pressure of Cl_2 above the melt was equal to the ambient. The silver chloride reference electrode consisted of a silver wire dipped into a 1 mol.% solution of AgCl in the NaCl-CsCl eutectic. The electrode potential of silver in this melt is described by the following equation (T in K):³⁹

$$E_{\text{Ag(I)/Ag}}^* = -1.223 + 3.26 \cdot 10^{-4} T (\pm 0.008) \text{ V} \quad [2]$$

Temperature was monitored using a K-type thermocouple in a beryllium oxide sheath and a silica capillary sampling tube was used for withdrawing a portion of the molten salt for further chemical analysis. Silica was used for the sheaths of the reference and counter electrodes and the bottom parts of the sheaths were closed with asbestos diaphragms. Asbestos was preliminary calcined at 973 K and the diaphragms were impregnated with the corresponding solvent salt prior to use. The melt was held in a glassy carbon crucible positioned in a silica cell, closed with a stopper containing all the necessary electrodes and attachments.

Formal standard electrode potentials of molybdenum were calculated from the experimentally measured potential values and molybdenum concentration determined by chemical analysis.

To determine molybdenum redox potentials, the potentiometric measurements were performed in the melts containing the products of reaction of molybdenum dioxide (or mixtures of molybdenum and molybdenum dioxide) with hydrogen chloride. In this case glassy carbon rods were used as working electrodes and with silver chloride electrode as the reference.

Cyclic voltammetry and chronopotentiometry measurements were also performed employing the Autolab PGSTAT 302N potentiostat. A silver chloride electrode was used here as the reference and a glassy carbon rod (2.48 mm dia.) sheathed from the sides by a beryllium oxide tube acted as a working electrode. The surface area of the working electrode was 0.048 cm^2 . A silica tube closed with a diaphragm and contained a molybdenum wire dipped into a MCl-PbCl_2 melt (M = alkali metal) served as a counter electrode. The surface area of the counter electrode was ca. 1.2 cm^2 . The design of the counter electrode allowed separating any counter electrode reaction from the bulk of the electrolyte.

Results and Discussion

Stability of Mo(III) ions in chloride melts.—Electronic absorption spectroscopy offers a convenient tool for monitoring processes involving Mo(III) species in fused salts. Molybdenum(III) containing chloride melts have characteristic electronic absorption spectra (EAS) in the visible region. The EAS contain two relatively intense absorption bands with clearly defined maxima around 580 and 440 nm and a weak shoulder around 680 nm, Fig. 1. The absorption bands originate from the electronic transitions in the six-coordinated MoCl_6^{3-} complex ions, i.e. two spin-allowed transitions ($^4A_{2g} \rightarrow ^4T_{1g}$ and $^4A_{2g} \rightarrow ^4T_{2g}$) and a spin forbidden transition $^4A_{2g} \rightarrow ^2T_{2g}$. Spectra recorded in the course of molybdenum anodic dissolution showed a steady absorbance increase. The concentration of molybdenum(III) ions (calculated using Beer's law and results of the chemical analysis of the final melt) linearly increased with time, Fig. 2.

The results of analysis of Mo(III) EAS in various chloride melts are summarized in Table I. Positions of the absorption bands were determined after resolving the spectra into constituent Gaussian bands except for the spectra taken from the literature where the peak positions reported by the authors or estimated from spectral curve profiles were used. Absorption bands shifted toward lower energy (higher wavelengths) upon increasing temperature or mean radius of the alkali metal cation. Ligand field splitting energy Dq also decreases with

Figure 1. EAS recorded during anodic dissolution of molybdenum in NaCl-CsCl melt at anodic current density of 0.006 A/cm², 823 K. Time after commencing dissolution (bottom to top, min): 2; 2.5; 4; 5.5; 7.5; 17.5; 20; 25.5; 31; 36; 41 and 46.

Figure 2. Changing Mo(III) concentration in NaCl-CsCl based melts during anodic dissolution of molybdenum from the results of EAS measurements, 923 K. Anodic current, A: 0.01 (1), 0.1 (2) and 0.275 (3).

temperature and cationic radius. Racah parameter B increases with the radius of the cation resulting in increasing the nephelauxetic parameter β characterizing the degree of “ionicity” of bonds in the complex ions. The value of β varies from ca. 0.7 to ca. 0.9 upon changing the melt cation from Li⁺ to Cs⁺. Racah parameter C was determined from

the energy of the low intensity spin-forbidden transition $^4A_{2g} \rightarrow ^2T_{2g}$ and the values obtained should be treated as approximate. No clear effect of temperature and melt composition on the value of this parameter was found. Ligand field stabilization energy δ of MoCl₆³⁻ ion decreases from LiCl to CsCl based melts indicating increasing stability of the complex ion due to lowering polarizing effect of the outer sphere cations.

Table I. Spectroscopic parameters of Mo(III) species in chloride melts.

Melt	Mean cation radius / Å	T / K	Bands maxima / nm			Dq / cm ⁻¹	B / cm ⁻¹	C / cm ⁻¹	β	δ / kJ/mol	Ref. ^b
			$^4A_{2g} \rightarrow ^2T_{2g}$	$^4A_{2g} \rightarrow ^4T_{2g}$	$^4A_{2g} \rightarrow ^4T_{1g}$						
emimAlCl ₄		298	685 ^a	544 ^a	439 ^a	1840	398	2030	0.65	263.9	40
LiCl	0.78 ^c	1023	661	564	448	1770	418	2120	0.68	254.3	-
		1123	721	588	462	1700	426	1870	0.7	244.1	-
NaCl	0.98 ^c	1123	741	591	445	1690	525	1700	0.86	242.9	-
LiCl-KCl	1.0 ^c	673	685	552	425	1810	505	1900	0.83	260.1	42
		1023	668	571	444	1750	463	2040	0.76	251.2	-
LiCl-KCl-CsCl	1.097 ^d	673	629	554	428	1810	494	2170	0.81	259.3	-
		773	696	567	434	1765	506	1870	0.83	253.4	-
		873	694	579	443	1730	496	1890	0.81	247.7	-
		973	695	581	445	1720	492	1895	0.8	247.2	-
		1073	701	584	449	1710	481	1890	0.79	245.8	-
NaCl-KCl	1.16 ^c	968	699 ^a	595 ^a	442 ^a	1680	559	1840	0.91	241.2	41
		973	684 ^a	583 ^a	436 ^a	1715	552	1890	0.9	246.2	8
		1023	699	584	446	1710	499	1880	0.82	245.7	-
KCl	1.33 ^c	1123	774	600	447	1670	547	1580	0.89	239.2	-
NaCl-KCl-CsCl	1.37 ^d	823	699	575	434	1740	539	1830	0.88	249.4	-
		923	703	581	440	1720	519	1840	0.85	247.1	-
		1023	701	586	451	1710	476	1890	0.78	245.0	-
NaCl-CsCl	1.43 ^c	788	696 ^a	558 ^a	433 ^a	1790	478	1890	0.78	257.4	41
		823	683	576	440	1740	505	1930	0.83	249.3	-
		873	701	581	443	1720	500	1860	0.82	247.1	-
		968	699 ^a	599 ^a	444 ^a	1670	561	1840	0.92	239.6	41
		1023	703	587	447	1705	498	1860	0.82	244.7	-
RbCl	1.49 ^c	1123	748	615	455	1625	552	1680	0.91	233.2	-
KCl-CsCl	1.53 ^d	1023	713	588	445	1700	517	1810	0.85	244.3	-
CsCl	1.65 ^c	965	699 ^a	592 ^a	446 ^a	1690	524	1860	0.86	242.5	41
		1023	703	591	446	1690	518	1850	0.85	243.0	-
		1123	755	622	457	1610	560	1660	0.92	230.9	-

^aEstimated without resolving the spectra into individual bands.

^bThe dash in the reference column indicates the results obtained in the present study.

^cTaken from Smirnov.¹⁰

^dCalculated here from the molar composition of the mixture.

Figure 3. Decreasing Mo(III) concentration in alkali chloride based melts held under argon atmosphere. Melt composition and temperature shown for each set of data.

Molybdenum chloro-ions have limited stability in fused alkali chlorides and the concentration of molybdenum(III) ions in high temperature chloride melts left under an inert atmosphere decreased over time. Electrochemical, chemical and spectroscopy studies showed that Mo(III) chloro-species in chloride melts can undergo disproportionation:^{26,42}

resulting in a gradually decreasing molybdenum concentration in the melt and precipitation of fine molybdenum metal particles. EAS measurements showed that Mo(III) concentration in the melt prepared by anodic dissolution of molybdenum metal or by dissolving K_3MoCl_6 , decreased over time and this decrease was essentially linear, Fig. 3. Molybdenum concentration in the melt was determined from the absorption values using Beer's law. The rate at which Mo(III) concentration decreased depended on temperature and cationic melt composition, the higher the temperature or smaller the cation, the faster the Mo(III) concentration dropped. The reaction rates determined for various melt compositions are summarized in Table II. The starting molybdenum(III) concentration in the melt was around 0.15–0.2 mol/kg and the reaction rates increased with temperature or decreasing alkali cation radius, showing that the equilibrium of Reaction 3 was shifted to the right at elevated temperatures or in the presence of cations with high ionic momentum. Such instability of Mo(III) containing melts complicates potentiometric measurements and can be one of the possible reasons for discrepancy in reported molybdenum electrode potential values.^{9–21}

Molybdenum electrode potentials in alkali chloride melts.—In the present study molybdenum powder was added to the melt during measurements to slow down the Reaction 3 and minimize its influence on the results. Potentials were taken as stationary if they did

Figure 4. Molybdenum formal standard electrode potentials in NaCl-CsCl (a), LiCl-KCl-CsCl (b) and NaCl-KCl (c) based melts. Cl^-/Cl_2 reference couple. Empty symbols – present work; solid symbol and lines – literature data.^{19–21}

not change by more than 5 mV over 30 minutes. Immediately after finishing recording the potentials, a sample of the melt was withdrawn into a sampling silica capillary tube, rapidly quenched and used for the further chemical analysis. Student's *t*-distribution with 95% confidence interval was used for the statistical analysis of the experimental data.

Individual alkali metal chlorides have relatively high melting points and therefore mixtures of low-melting or eutectic compositions are preferred for technological applications. In the present study, three mixtures were selected, i.e. NaCl–KCl (inexpensive but relatively high melting); NaCl–CsCl (low-melting and non-hygroscopic but expensive); and LiCl–KCl–CsCl (having the lowest melting point amongst all alkali chloride mixtures). The results obtained are presented in Fig. 4 where they are also compared with the available literature data. The following equations were obtained by the linear least squares fitting and describe the temperature dependencies of the formal standard electrode potentials of molybdenum:

$$E^*_{\text{Mo/Mo(III)}} = -1.727 + 8.65 \cdot 10^{-4} \cdot T (\pm 0.04) \text{ V (NaCl-CsCl, 793 – 1023 K)} \quad [4]$$

$$E^*_{\text{Mo/Mo(III)}} = -1.327 + 4.46 \cdot 10^{-4} \cdot T (\pm 0.04) \text{ V (NaCl-KCl, 973 – 1123 K)} \quad [5]$$

$$E^*_{\text{Mo/Mo(III)}} = -1.405 + 6.05 \cdot 10^{-4} \cdot T (\pm 0.04) \text{ V (LiCl-KCl-CsCl, 633 – 1173 K)} \quad [6]$$

Table II. Rate of Reaction 3 in alkali chloride based melts.

Melt	T / K	Starting Mo(III) conc.		Reaction rate	
		mol kg ⁻¹	mol dm ⁻³	mol kg ⁻¹ s ⁻¹	mol dm ⁻³ s ⁻¹
LiCl	1023	0.0205	0.0294	$1.38 \cdot 10^{-6}$	$1.98 \cdot 10^{-6}$
LiCl-KCl	1023	0.0169	0.0251	$1.30 \cdot 10^{-6}$	$1.94 \cdot 10^{-6}$
NaCl-KCl	1023	0.0166	0.0257	$7.51 \cdot 10^{-7}$	$1.17 \cdot 10^{-6}$
NaCl-KCl-CsCl	923	0.0158	0.0380	$4.49 \cdot 10^{-7}$	$1.08 \cdot 10^{-6}$
	1023	0.0221	0.0513	$6.09 \cdot 10^{-7}$	$1.41 \cdot 10^{-6}$
NaCl-CsCl	823	0.0156	0.0401	$1.90 \cdot 10^{-7}$	$4.88 \cdot 10^{-7}$
	1023	0.0143	0.0339	$5.12 \cdot 10^{-7}$	$1.21 \cdot 10^{-6}$
KCl-CsCl	1023	0.0194	0.0478	$7.76 \cdot 10^{-7}$	$1.92 \cdot 10^{-6}$
CsCl	1023	0.0134	0.0359	$1.28 \cdot 10^{-7}$	$3.43 \cdot 10^{-7}$

Table III. Molybdenum formal standard electrode potentials in fused alkali metal chlorides (Cl⁻/Cl₂ reference couple).

Melt	$E^*_{\text{Mo/Mo(III)}}$ at 1123 K / V (present work)	$E^*_{\text{Mo/Mo(III)}}$ at 1100 K / V ^{9-13,15,16}
LiCl	-0.720 ± 0.040	-0.754
NaCl	-0.780 ± 0.040	
KCl	-0.810 ± 0.020	-1.067
RbCl	-0.843 ± 0.035	
CsCl	-0.877 ± 0.005	-1.113

The potential values shift in a negative direction with increasing mean radius of the alkali cation. The results obtained here for NaCl-CsCl eutectic-based melt agree closely with the earlier work.²¹ For the NaCl-KCl mixture, the results obtained by Aleksandrov et al.²⁰ were around 60–70 mV more positive than found here, while the single point reported by Baraboshkin¹⁹ at 973 K was even more positive.

The temperature dependencies of the Gibbs free energy change of MoCl₃ formation in the melts studied were calculated from the temperature dependencies of the formal standard electrode potentials using the standard relation between the free energy and the electrochemical cell emf,³⁸ and the following equations were derived:

$$\Delta G^*_{\text{MoCl}_3} = -499.9 + 250.4 \cdot 10^{-3} \cdot T (\pm 3) \text{ kJ/mol (NaCl-CsCl, 793 – 1023 K)} \quad [7]$$

$$\Delta G^*_{\text{MoCl}_3} = -384.1 + 129.1 \cdot 10^{-3} \cdot T (\pm 4) \text{ kJ/mol (NaCl-KCl, 973 – 1123 K)} \quad [8]$$

$$\Delta G^*_{\text{MoCl}_3} = -406.7 + 175.2 \cdot 10^{-3} \cdot T (\pm 1) \text{ kJ/mol (LiCl-KCl-CsCl, 633 – 1173 K)} \quad [9]$$

Electrode potentials of metals in fused chlorides depend on the cationic composition of the melts. Alkali metal cations form second coordination sphere around the transition metal centres and have the effect on the stability of the complexes and electrochemical and thermodynamic properties of the metal species in the melts. As shown above, the stability of Mo(III) chloro-species in alkali chloride metal decreases with decreasing alkali metal cation radius (increasing ionic momentum). To study the effect of the nature of alkali cations on molybdenum electrochemical properties, the electrode potentials were measured in the melts based on individual alkali chlorides at the same temperature. The formal standard electrode potentials determined here are presented in Table III. The following equation obtained by the linear least squares fitting of the experimental data describes the dependence of molybdenum electrode potential in fused individual alkali chlorides on the cation radius at 1123 K:

$$E^*_{\text{Mo/Mo(III)}} = 0.239/r_{\text{cation}} - 1.02 (\pm 0.03) \text{ V} \quad [10]$$

Increasing the cation radius shifted the potential in the negative direction in agreement with previous reports.^{9-14,16} However, the $E^*_{\text{Mo/Mo(III)}}$ values obtained in the present study were more positive than those given by Smirnov and Ryzhik at a comparable temperature, Table I, with the difference exceeding in some cases 200 mV.

Analysis of the literature⁹⁻²¹ showed that there is some discrepancy between the results obtained by various authors. The data available for various melts are compared in Fig. 5, where $E^*_{\text{Mo/Mo(III)}}$ is presented as a function of cationic radius at 1123 K. For individual alkali chlorides the effective ionic radii were used.^{10,43} For binary or ternary alkali chloride mixtures, the mean cationic radius was calculated from the molar composition of the corresponding mixture. If the measurements of molybdenum electrode potentials reported in the literature were performed below 1123 K, the potential value presented in Fig. 5 was calculated using the potential temperature dependencies reported by the authors of the corresponding investigations. With the exception of

Figure 5. Formal standard electrode potentials of molybdenum (vs. Cl⁻/Cl₂ couple) in fused alkali chlorides at 1123 K. The melts are positioned according to the average cationic radii. Circles – present work; crosses – data from the literature.⁹⁻²¹

those reported by Ryzhik and Smirnov for CsCl, KCl and LiCl-KCl based melts^{11-13,15,16} there is a satisfactory agreement (normally within ±50 mV) between the data reported. Molybdenum electrode potential values obtained by Ryzhik and Smirnov were far more negative than any other available data and are likely erroneous.

Molybdenum redox potentials in alkali chloride melts.—Although molybdenum(IV) and (V) chloro-species can be formed in alkali chloride melts, very little is known about their electrochemical properties. Melts containing Mo(IV) ions can be obtained by reacting MoO₂ with hydrogen chloride.³¹ Our previous spectroscopic and spectroelectrochemistry studies showed that Mo(IV) chloro-species are most stable at lower temperatures and in the melts containing low ionic momentum cations (cesium).³¹ Electronic absorption spectroscopy allowed clear distinction between Mo(III) and Mo(IV) ions. Examples of the EAS of the melts containing the products of reaction of MoO₂ with HCl at various temperatures are presented in Fig. 6. The spectra recorded at 823 and 873 K contain a well pronounced peak around 13,000 cm⁻¹, as well as a hidden band around 16,100 cm⁻¹ and a low energy edge of a band with the maximum above 20,000 cm⁻¹, cf. top and middle spectra in Fig. 6. The mean oxidation state of molybdenum in these melts determined by redox titration was close to four. Analysis of the possible electronic transitions for d² electronic configuration showed that these bands correspond to the following transitions in the MoCl₆²⁻ complex ion (in order of increasing energy): ³T_{1g} → ³T_{2g}, ³T_{1g} → ¹A_{1g}, ³T_{1g} → ³T_{1g} (P). The second transition is spin-forbidden and therefore the intensity of the corresponding band is lower than for the spin-allowed transitions. The spectra recorded at 923 K contained more bands, cf. bottom spectrum in Fig. 6. The mean oxidation state of molybdenum in this melt determined oxidimetrically was 3.40 ± 0.03. The melt therefore contained a mixture of Mo(IV) and Mo(III) ions and the EAS contained a superposition of the absorption bands corresponding to the electronic transitions in MoCl₆²⁻ (d²-configuration) and MoCl₆³⁻ (d³-configuration) complex ions. The resolved bands corresponded to the following transitions (in order of increasing energy): ³T_{1g} → ³T_{2g} (in MoCl₆²⁻), ⁴A_{2g} → ²T_{2g} (in MoCl₆³⁻), ⁴A_{2g} → ⁴T_{2g} (in MoCl₆³⁻), ⁴A_{2g} → ⁴T_{1g} (in MoCl₆³⁻). The ⁴A_{2g} → ²T_{2g} transition is forbidden by spin and the corresponding band has low intensity. The band corresponding to the ³T_{1g} → ¹A_{1g} spin-forbidden transition in MoCl₆²⁻ ion is masked by an intense band of ⁴A_{2g} → ⁴T_{2g} transition in MoCl₆³⁻ ion and could not be resolved with confidence.

Thus, depending on temperature, the reaction of MoO₂ with HCl produced either Mo(IV) or a mixture of Mo(IV) and Mo(III) ions. The latter were formed as the result of disproportionation of Mo(IV)

Figure 6. EAS of NaCl-KCl-CsCl eutectic based melts containing the products of reaction of MoO₂ with HCl. Experimental conditions: 823 K, 10 min reaction time (a); 873 K, 11 min reaction time (b); 923 K, 1 min reaction time (c). Electronic transitions and ions are shown for each band.

species and the following reactions describe the process of MoO₂ chlorination by HCl in a chloride melt:

Molybdenum oxychloride (MoOCl₂) having a low boiling point sublimed (at least partially) from the melt and condensed in the form of yellow needles in the upper cold part of the experimental cell. Increasing temperature favored Reactions 13 and 14. The high vapor pressure of molybdenum(V) chloride assists its sublimation from the melt. A dark blue solid condensed in the upper part of the cell during the experiments at 650°C indicated the formation of MoCl₅.

In a preliminary study,³¹ high temperature spectroscopy and spec-troelectrochemistry measurements showed that Mo(III)/Mo(IV) oxida-tion/reduction was a reversible process, and Mo(III)/Mo(IV) redox potential was estimated from the results of spec-troelectrochemistry in NaCl-CsCl eutectic. At 823 K the potential found was $-(0.83 \pm 0.04)$ V vs. Cl⁻/Cl₂ or 0.45 ± 0.04 V vs. Ag/AgCl reference electrode. In the present work, potentiometry measurements on an inert (glassy carbon) electrode were employed to determine $E^*_{Mo(III)/Mo(IV)}$ redox potentials. Chlorination of molybdenum metal by hydrogen chloride resulted in the melts containing only Mo(III) ions. Therefore, melts

containing a mixture of Mo(III) and Mo(IV) ions were prepared by reacting a mixture of Mo and MoO₂ with HCl. The results obtained in NaCl-CsCl and NaCl-KCl-CsCl based melts are summarized in Table IV. The primary factor affecting the value of Mo(III)/Mo(IV) redox potential is the ratio of Mo(IV) and Mo(III) concentrations in the melt, which in turn was calculated from the oxidimetrically determined mean oxidation state of molybdenum in the melt. Increased temperature resulted in a significant decreasing mean oxidation state with Mo(III) ions becoming predominant. The oxidimetric titration is, by its nature, not a very precise method as are all titrimetry techniques. Direct potentiometry measurements produced rather scattered data due to considerable uncertainty in determining mean oxidation state of molybdenum in the melt by redox titration (Table IV). Therefore the values of $E^*_{Mo(III)/Mo(IV)}$ redox potentials given in Table IV should be considered as estimates. Analysis of the $E^*_{Mo(III)/Mo(IV)}$ values obtained, and comparison with the $E^*_{Mo/Mo(III)}$ electrode potentials allowed, at the present stage, the derivation of the following equations of temperature dependencies of the formal standard redox potentials Mo(III)/Mo(IV) vs. Cl⁻/Cl₂ couple:

$$E^*_{Mo(IV)/Mo(III)} = -1.24 + 5.51 \cdot 10^{-4} T \text{ (NaCl-CsCl, 823 – 923 K)} \quad [15]$$

$$E^*_{Mo(IV)/Mo(III)} = -0.97 + 3.08 \cdot 10^{-4} T \text{ (NaCl-KCl-CsCl, 823 – 973 K)} \quad [16]$$

Cyclic voltammetry was next employed to study molybdenum re-dox behavior. Gabriel et al.⁴² noted that cyclic voltammograms (CVs)

Table IV. Results of potentiometric measurements of Mo(III)/Mo(IV) redox potentials in chloride melts.

T/K	Mo concentration/wt%	n_{ox}	GC electrode potential ^a / V	[Mo(VI)] / [Mo(III)]	$E^*_{\text{Mo(III)/Mo(IV)}}$ ^b / V
NaCl-CsCl eutectic melts					
823	1.44	3.90 ± 0.04	0.478	10.7 ± 5.0	-0.962 ± 0.036
	2.582	3.64 ± 0.05	0.255	1.8 ± 0.4	-1.068 ± 0.016
873	1.668	3.04	0.363	0.04	-0.683
923	1.991	3.06 ± 0.02	0.298	0.06 ± 0.03	-0.755 ± 0.041
973	2.145	3.04	0.006	0.04	-1.019
NaCl-KCl-CsCl eutectic melts					
823	2.016	3.15	0.332	0.18	-0.724
	0.358	3.75 ± 0.02	0.262	3.03 ± 0.33	-0.996 ± 0.008
873	1.450	3.24 ± 0.01	0.276	0.31 ± 0.01	-0.820 ± 0.002
	1.336	3.34 ± 0.14	0.491	0.57 ± 0.32	-0.637 ± 0.048
	1.354	3.11 ± 0.01	0.299	0.12 ± 0.02	-0.728 ± 0.008
923	0.913	3.11 ± 0.04	0.261	0.12 ± 0.04	-0.755 ± 0.031
	0.969	3.42 ± 0.08	0.273	0.75 ± 0.25	-0.889 ± 0.028
973	1.596	3.01	0.208	0.01	-0.602
	2.837	3.04 ± 0.01	0.200	0.04 ± 0.01	-0.739 ± 0.010
	1.058	3.07 ± 0.03	0.218	0.07 ± 0.04	-0.740 ± 0.053

^a vs. Ag/AgCl (1 mol. % in NaCl-CsCl);^b vs. Cl^-/Cl_2 .

recorded in LiCl-KCl- K_3MoCl_6 melts contained only one reduction peak attributed to a three-electron reduction of Mo(III) and a corresponding oxidation peak. Close examination of the CV presented by Gabriel et al.⁴² however showed that there were one additional cathodic peak at the potential about 1.2 V more positive than Mo(III)-to-Mo(0) reduction and one anodic peak, ca. 0.6 V more positive than Mo(0)-to-Mo(III) oxidation. It was, therefore, of interest to investigate this process in more detail. In the present study the experiments were performed in NaCl-CsCl and NaCl-KCl-CsCl based melts at 823 and 923 K. Examples of CVs recorded are presented in Fig. 7. The potential was scanned first in the anodic direction followed by a cathodic scan. The shape of the voltammograms is characteristic for a redox process involving soluble oxidized and reduced species. The anodic and cathodic waves have more positive potentials than the waves of Mo(III)↔Mo metal reduction/oxidation. The potentials also correspond to the values obtained in potentiometric measurements in Mo(III)+Mo(IV) containing melts, Table IV.

Analysis of the cyclic voltammograms showed that the peak current is directly proportional to the square root of the scan rate and at

low scan rates anodic and cathodic potentials are independent of the scan rate, Fig. 8. The anodic and cathodic processes are, therefore, controlled by diffusion of the electroactive species. The number of electrons (n) was calculated from the difference of peak and half-peak potentials (E_P and $E_{P/2}$):

$$E_P - E_{P/2} = -2.2 \cdot R \cdot T / (n \cdot F) \quad [17]$$

The value of n obtained for the scan rates below 0.2 V/s was 1.05 ± 0.15 for the cathodic reaction and 1.10 ± 0.15 for the anodic reaction. The cyclic voltammograms recorded were therefore assigned to a one-electron Mo(III)↔Mo(IV) oxidation-reduction process. Formal standard redox potentials of the Mo(III)/(IV) couple were estimated from the results of cyclic voltammetry measurements using the half-peak potential.⁴⁴

$$E_{1/2} = E^0_{\text{Mo(III)/Mo(IV)}} + \frac{R \cdot T}{F} \cdot \ln \left(\frac{D_{\text{Mo(III)}}}{D_{\text{Mo(IV)}}} \right)^{1/2} + \frac{R \cdot T}{F} \cdot \ln \left(\frac{\gamma_{\text{Mo(III)}}}{\gamma_{\text{Mo(IV)}}} \right) \quad [18]$$

Figure 7. Cyclic voltammograms recorded in molybdenum containing melts. Glassy carbon working electrode, 0.048 cm^2 ; Ag/AgCl reference; Pb/PbCl₂ counter electrode. Scan rate, V s^{-1} (inner to outer): 0.02; 0.04; 0.06; 0.08; 0.1; 0.2; 0.5; 1 and 2. Experimental conditions: (a) NaCl-KCl-CsCl, 923 K, 0.92 wt% Mo; (b) NaCl-CsCl, 823 K, 1.07 wt% Mo. Arrows show the starting point and direction of the potential scan.

Figure 8. The effect of scan rate on anodic and cathodic currents in cyclic voltammograms (a) and anodic and cathodic peak potentials (b). Electrodes as in Fig. 7. Experimental conditions: (a) NaCl-KCl-CsCl, 923 K, 0.92 wt% Mo; (b) NaCl-CsCl, 823 K, 1.07 wt% Mo.

Table V. Molybdenum(III)/(IV) formal standard redox potentials obtained from the results of cyclic voltammetry measurements, Cl^-/Cl_2 reference couple.

Melt	T / K	Mo concentration / wt%	$E^*_{\text{Mo(III)/Mo(IV)}} / \text{V}$
NaCl-CsCl	823	0.17	-0.811 ± 0.008
		0.27	-0.806 ± 0.006
		0.68	-0.868 ± 0.013
		1.07	-0.865 ± 0.013
NaCl-KCl-CsCl	833	0.85	-0.867 ± 0.010
		0.98	-0.873 ± 0.006
	923	0.13	-0.902 ± 0.008
		0.30	-0.950 ± 0.020
		0.92	-1.096 ± 0.025

In dilute solutions the activity coefficients of dissolved species (γ) remain essentially constant. Standard potential E^0 can therefore be changed to the formal standard potential E^* :

$$E^*_{\text{Mo(III)/Mo(IV)}} = E^0_{\text{Mo(III)/Mo(IV)}} + \frac{R \cdot T}{F} \cdot \ln \left(\frac{\gamma_{\text{Mo(III)}}}{\gamma_{\text{Mo(IV)}}} \right) \quad [19]$$

To make an estimate of the formal standard redox potentials, the diffusion coefficients of the reduced and oxidized species are often taken as very close and the following equation is used:⁴⁴

$$E^*_{\text{Mo(III)/Mo(IV)}} \approx E_{1/2} = \frac{E_p^c + E_p^a}{2} \quad [20]$$

The results obtained are summarized in Table V. The redox potential values are more positive than molybdenum electrode potentials, as expected. The $E^*_{\text{Mo(III)/Mo(IV)}}$ redox potentials estimated from the results of cyclic voltammetry are, however, more negative than those obtained by potentiometry (*cf.* Tables IV and V). More accurate deter-

mination of molybdenum redox potentials would require information on the diffusion coefficients of the molybdenum species.

Diffusion coefficients of molybdenum ions in alkali chloride melts.—Several transient electrochemical techniques can be utilized for determining molybdenum species diffusion coefficients in molten salts. Molybdenum containing melts based on the ternary LiCl-KCl-CsCl eutectic were here studied using chronopotentiometry, and molybdenum ions diffusion coefficients were determined employing Sand's equation:^{42,45}

$$i \cdot \tau^{1/2} = \frac{1}{2} \cdot n \cdot F \cdot A \cdot \pi^{1/2} \cdot C \cdot D^{1/2}, \quad [21]$$

where i is the current, A; τ the transition time, s; n the number of electrons; F the Faraday constant, C/mol; A the plane electrode surface area, cm^2 ; C the concentration of the reactant, mol/cm^3 ; and D the diffusion coefficient of the reactant, cm^2/s . The results are presented in Table VI, where they are compared with the data available for LiCl-KCl eutectic based melts. The agreement between the results is good; the diffusion coefficients increase with temperature and decreasing radius of alkali cation. In LiCl-KCl-CsCl melt the following equation describes the temperature dependence of Mo(III) ions diffusion coefficients:

$$\log D_{\text{Mo(III)}} = -3702.3/T - 0.9 (\pm 0.3) \quad [22]$$

For a flat working electrode the Randles-Sevcik equation can be employed to calculate the diffusion coefficients of the electroactive species:⁴⁶

$$i_p = 0.4463 \cdot n^{3/2} \cdot F^{3/2} \cdot A \cdot C \cdot v^{1/2} \cdot D^{1/2} / (R \cdot T)^{1/2}, \quad [23]$$

where i_p is the peak current, A; v the potential scan rate, V/s; R the universal gas constant, J/(mol · K); T temperature, K; and n , F , A , C and D are the same as in Eq. 21. Diffusion coefficients of Mo(III) ions in NaCl-CsCl eutectic melts were determined from the analysis of the anodic waves of cyclic voltammograms and are included in Table VI. As expected, the diffusion coefficients increase with temperature or decreasing mean alkali cation radius. Analysis of the cathodic parts of

Table VI. Diffusion coefficients of molybdenum(III) chloro-ions in alkali chloride melts.

T, K	LiCl-KCl		LiCl-KCl-CsCl		NaCl-CsCl	
	$D_{\text{Mo(III)}} \cdot 10^5 / \text{cm}^2/\text{sec}$	Source	$D_{\text{Mo(III)}} \cdot 10^5 / \text{cm}^2/\text{sec}$	Source	$D_{\text{Mo(III)}} \cdot 10^5 / \text{cm}^2/\text{sec}$	Source
773	0.80 ± 0.05	42	0.19	present work	0.37 ± 0.14	present work
823						
873	1.43	26				
923			1.69	present work		
1023			2.53	present work		

the CVs allowed the estimation of Mo(IV) diffusion coefficients. In the NaCl-CsCl melt at 823 K the diffusion coefficient thus obtained was $(0.58 \pm 0.28) \cdot 10^{-6} \text{ cm}^2/\text{sec}$, which is about 6 times less than the diffusion coefficient of Mo(III) ions.

Conclusions

The electrochemical behavior of molybdenum was studied in alkali chloride melts by stationary and transient electrochemical techniques and the speciation of molybdenum(III) and (IV) ions were characterized by electronic absorption spectroscopy. EAS measurements were also employed to assess the stability of Mo(III) ions in high temperature chloride melts. Increasing temperature or increasing ionic momentum of the melt cation decreases the stability of Mo(III) chloro-species and the rate of Mo(III) disproportionation reaction increases by an order of magnitude upon changing the melt from CsCl to LiCl.

Formal standard electrode potentials of molybdenum were determined in a variety of alkali chloride based melts (individual chlorides and their mixtures) and compared with the data available in the literature. Increasing temperature or decreasing alkali cation radius shift $E^*_{\text{Mo/Mo(III)}}$ in a positive direction. Changing temperature by 540 degrees results in a potential shift of about 300 mV (for LiCl-KCl-CsCl melt) and switching from LiCl to CsCl alters the potential by ca. 150 mV.

Molybdenum(III)/(IV) redox potentials were measured employing potentiometry and cyclic voltammetry and found to be 0.2–0.3 V more positive than Mo/Mo(III) electrode potentials. The stability of Mo(IV) chloro-species decreases with temperature and at 923 K and above they undergo disproportionation into molybdenum(III) and (V) chlorides.

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