Defined Intercalation Stages from Cathodic Reduction of MoS₂ in Organic Electrolytes

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Cathodic reduction of MoS₂ in DMSO electrolytes containing alkali cations A⁺ results in the formation of defined ternary phases A⁺₀.₁₂₅(DMSO)₀.₆₅(MoS₂)₀.₁₂₅ with highly mobile solvated interlayer cations. Reduction of MoS₂ in DME electrolytes yields similar products. Basal spacings are dependent on solvent type and on ionic radius of A⁺. Further reduction of these compounds is associated with irreversible processes.

Introduction

The intercalation of alkali and alkaline earth metals into layered transition metal dichalcogenides MX₂ (M = metal, X = S, Se) of group IVb to group VIIb elements has first been reported by RÜDORFF. Bonding between the alkali atoms A and the chalcogenide layers in the resulting compounds AₓMX₂ is essentially of ionic character.

Later work established that chemical or electrochemical reduction of the dichalcogenides may lead either to the ternary phases AₓMX₂ or to solvated products Aₓ(solv)ₓ[MX₂], depending on the nature of the electrolyte. The intercalation compounds have attracted considerable attention with respect to electric properties (superconduction) and to potential application as cathode materials in secondary high energy density Li-batteries.

Group IVb and Vb dichalcogenides in general can be reduced easily as the standard potentials of the compounds are not far from zero, thus allowing even the use of protic solvents such as water. Reduction of group VI dichalcogenides, however, requires strong reducing agents and reactions have to be carried out in solvents which are rather stable towards cathodic decomposition. In this communication we report on the electrochemical reduction of MoS₂ and WS₂ in dimethylsulfoxide (DMSO) and 1,2-dimethoxyethane (DME) electrolytes.

A decisive advantage of the electrochemical method as compared to chemical reduction is the possibility to prepare definite intercalation stages provided the reduction of weighed samples is performed under controlled current conditions. The potential of the MX₂ electrode is a reference for the progress of the intercalation; at very low current densities this potential is close to the equilibrium value. If in the course of the reduction compounds with distinct difference in energy are formed successively, the potential of the MX₂ electrode changes stepwise. From these steps stoichiometric relationships can be calculated.

Results and Discussion

Potential-time curves of the galvanostatic reduction of 2 H-MoS₂ (converted to charge transferred per mg MoS₂) in solutions of Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ salts in dimethylsulfoxide (DMSO) are shown in Fig. 1.
Fig. 1. Galvanostatic reduction of MoS$_2$ pressed powder electrodes in CsI, RbI, KPF$_6$, NaBF$_4$, LiClO$_4$/DMSO. i = 100–150 $\mu$A $\cdot$ cm$^{-2}$; concentration of solutes $\leq$ 1 M.

For all ions except Li$^+$ a sharp step in potential is found close to 75 mAs $\cdot$ mg$^{-1}$ MoS$_2$ corresponding to a ratio A$^+$:MoS$_2$ = 1:8 or a tentative composition A$_{0.125}$MoS$_2$ of the product. The calculation of stoichiometries from the amount of charge consumed until a step in potential is reached is only valid on the assumption that (i) no current loss arises by side reactions and that (ii) the intercalation proceeds at a rate which allows a quasi-equilibrium distribution of A$^+$ in the host lattice at any time. These two conditions are to some extent conflicting as with increasing current density, i.e. increasing reaction rate, condition (ii) may no longer apply (charge transfer required to produce a step decreases) whereas with decreasing current density the background current caused by side reactions becomes relatively more important (charge transfer required to produce a step increases). Studies at different current densities in the system MoS$_2$/DMSO electrolyte demonstrated, however, that both conditions are accomplished in the current range investigated.

The position of the potential step at A$^+$:MoS$_2$ = 1:8 e.g. in NaBF$_4$/DMSO turned out to be almost independent on current density i for 200 < i < 2000 $\mu$A $\cdot$ cm$^{-2}$ geom. surface.

X-ray investigations of the reaction products obtained after the theoretical charge transfer calculated for A$_{0.125}$MoS$_2$ revealed that the basal spacings (i.e. the distances between neighbouring MoS$_2$ layers) of these phases range between 14.51 Å and 18.02 Å (Table I). Basal spacings of the RUDORFF intercalation compounds A$_n$MoS$_2$ range between 7.50 Å for Na$_{0.6}$MoS$_2$ and 8.89 Å for Cs$_{0.5}$MoS$_2$. It is known from investigations of related phases by Danot that variation of $x$ results in relatively small changes only for the basal spacing. The high spacing values observed on reduction in DMSO electrolyte thus indicate clearly that the solvent has been taken up into the interlayer space along with the alkali cations. Compounds of similar type have been reported before and were prepared by solvation of RUDORFF phases A$_n$MoS$_2$; they exhibit typical polyelectrolyte character. The spacings of both compound series agree well, e.g. the sodium phase Na$_{0.1}^+$ (DMSO)$_n$[MoS$_2$]$^{0.1^-}$ resulting from solvation of the corresponding alkali metal intercalation compounds gives a basal spacing of 18.79 Å; the sodium phase prepared on cathodic reduction of MoS$_2$ in DMSO/NaBF$_4$ shows a spacing of 18.76 Å (Table I). The products obtained from reduction in the organic alkali salt solutions are thus to be considered as polyelectrolytes A$_n^+$(DMSO)$_n$[MoS$_2$]$^{0.1^-}$ consisting of a negatively charged MoS$_2$ multilayer matrix with solvated alkali cations between the metal chalcogenide sheets.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Basal spacing (Å)</th>
<th>Interlayer spacing (Å)</th>
<th>Radius A$^+(\text{DMSO})_n$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>14.51</td>
<td>8.36</td>
<td>4.0**</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>18.76</td>
<td>12.61</td>
<td>3.2*</td>
</tr>
<tr>
<td>K$^+$</td>
<td>17.68</td>
<td>11.53</td>
<td>3.0*</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>17.88</td>
<td>11.73</td>
<td>2.85**</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>18.02</td>
<td>11.87</td>
<td>2.7**</td>
</tr>
</tbody>
</table>

* Ref. 7.
** Calculated from single ion conductivities at infinite dilution (ref. 8).
Basal spacings $d$ are dependent on the alkali cation $A^+$ in the two-dimensional organic solvate phase (Table I). The highest value of $d$ is found for the sodium compound. $K^+$, $Rb^+$, and $Cs^+$ phases – i.e. derivatives of cations with lower energy of solvation as compared to sodium – exhibit somewhat lower $d$ values; a slight increase is observed for $d$ with increasing ionic radius from $K^+$ to $Cs^+$. The interlayer spacing of the lithium compound which amounts to 14.51 Å is remarkably small which correlates with the exceptional behaviour of $\text{MoS}_2$ in $\text{Li}^+/$DMSO electrolyte (cf. below).

The correlation between potentials measured during the galvanostatic intercalation of ions $I$ into a solid $S$ and the equilibrium potentials of $I^+_S$ is increasing with increasing mobility of $I$ in $S$ (lower concentration polarization) and with decreasing activation energy of the intercalation (lower activation polarization). Since the specific conductivities of DMSO electrolytes are high, the polarization in the liquid phase may be neglected at current densities up to some mA cm$^{-2}$. The mobility of the cations $A^+$ in $A_{x^+}(\text{DMSO})_y[\text{MoS}_2]^z$ must be considerable for compounds with $A^+:\text{MoS}_2 = 1:8$. This can be estimated from the nearly rectangular shape of the potential/charge curves in Fig. 1. As a low mobility of the cations $A^+$ would result in a nonuniform distribution within the host lattice, the potentials measured in this case should be expected to differ from the equilibrium potential of one definite compound and to present a mixed potential which in addition might be falsified by a large diffusion polarization. Potential-charge curves under these conditions should be characterized by a more or less continuous slope instead of a significant sharp step.

The existence of a quasi-equilibrium distribution of $A^+$ in the course of a galvanostatic electrolysis can be controlled by the effect of current interruption on potential. For a “high mobility intercalate” forming one defined phase in a reversible reaction, the potential drop expected should be fast and small. In case of a slow internal equilibration of the intercalate species an equivalent slow drift in potential should result. An examination of the $\text{MoS}_2$ reduction in KPF$\text{e}$/DMSO showed that the potential in the range $0 < x < 0.125$ remains practically constant after interruption (= low activation and concentration polarization), whereas for $x > 0.125$ the potential drifts substantially to more positive values.

The coulombic efficiency of a galvanostatic reoxidation of $A_{0.125}(\text{DMSO})\text{MoS}_2$ is low as is already indicated by the low peak area of the reoxidation peak in Fig. 2a compared to that of the cathodic half cycle. The difference to 100% current yield, however, is not due to a half life time of the $\text{MoS}_2$ intercalation compound in the order of the time required for a single sweep but must originate from kinetic hindrance of the reoxidation reaction.

![Fig. 2a. Cyclic voltammogram of Pt and $\text{MoS}_2$ in 1 M KPF$\text{e}$/DMSO. $v = 600$ mV min$^{-1}$. Working electrode not sandwiched.](image1)

![Fig. 2b. Cyclic voltammogram of $K_{0.125}(\text{DMSO})\text{MoS}_2$ in 1 M KPF$\text{e}$/DMSO. $v = 150$ mV min$^{-1}$. Working electrode sandwiched between porous glass; potentials include reasonable IR drop.](image2)
This may be concluded from decreasing current yield with increasing amount of MoS$_2$ reacted. Variation of the wet-stand time of the reduced electrode showed only little influence on the current yield. Similar effects have been found for redox reactions of other layered electrode materials \textit{e.g.} MoO$_3$.

An exceptional behaviour is observed on cathodic reduction of MoS$_2$ in DMSO/LiClO$_4$. Li$^+$ is the only cation in the alkali series which does not show a distinct potential step at $x = 0.125$. A clear step is found, however, if the LiClO$_4$/DMSO electrolyte is saturated with dry ammonia at room temperature. The addition of NH$_3$ also results in a shift of the potential from the uncommonly negative value in pure LiClO$_4$/DMSO to a value close to $-1.5$ V vs SCE which is found for the other alkali ions in DMSO*. Although there is no conclusive proof, this behaviour is probably due to kinetic effects. The effective radii of solvated alkali metal cations in DMSO solutions are known to decrease steadily from 4.0 Å to 2.7 Å in the order Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, whereas an outstanding low value is found for the Li$^+$ compound (Table I). It is reasonable to assume that in the presence of NH$_3$ Li$^+(\text{DMSO})_{n-x}$(NH$_3$)$_m$ species with a mixed solvation sphere are existing which have smaller effective radii and a lower activation energy for intercalation as compared to Li$^+(\text{DMSO})_n$. The interlayer spacing of the Li-compound (14.51 Å) is obviously controlled only by the steric requirements of the DMSO molecules as there is no significant influence of NH$_3$ addition on the basal spacing.

Potential curves for reduction of MoS$_2$ in DMSO electrolytes beyond the stage A$_{0.125}$(DMSO)MoS$_2$ are characterized by a slope and sometimes additional inflection points. This is indicative for a further reduction of the solid electrode; solvent reduction itself occurs at a much more negative but constant potential. Catalytic decomposition of the solvent may occur, however, at potentials within the – only kinetically controlled – range of its electrochemical stability at inert electrodes. In-

* Strictly speaking, potentials vs SCE in different electrolytes may not be compared because of different liquid junction potentials at the phase boundary aqueous/organic. In the case of 1:1 salts of similar and high concentration in the same organic solvent these differences, however, should be very small.

stability of products towards formation of A$_3$S has also to be taken into consideration. Unsolvated Li$_3$MoS$_2$ \textit{e.g.} is expected to be stable for low values of $x$ only, whereas at higher $x$ values the compound should be unstable relative to Li$_4$S formation.

The presence of a second stage in the reduction of MoS$_2$ is suggested by the results of cyclic voltammetry (CV). Starting with MoS$_2$ in KPF$_6$/DMSO only one reversible reaction (reoxidation peak [I] in Fig. 2a) can be observed, the reaction indicated at lower potential is irreversible solvent decomposition at the Pt electrode. When K$_{0.123}$DMSO)MoS$_2$ prepared previously is used directly as electrode and the reoxidation reaction is limited by the sweep range, a second reversible peak [II] is occurring (Fig. 2b). The area of the reoxidation peak [II] is nearly independent on the preceeding cathodic load and therefore this second reversible peak cannot be due to a stable compound.

Powder diagrams of compounds obtained on reduction beyond $x = 0.125$ indicate the formation of decomposition products along with the pattern noted for the phases A$_{0.125}$(DMSO)MoS$_2$.$^{3,125-}$ Weak lines belonging to molybdenum metal have been identified in some of the products. On reduction of MoS$_2$ and WS$_2$ in KPF$_6$/DMSO and of MoS$_2$ in LiClO$_4$/DMSO saturated with NH$_3$ solvent decomposition was not observed until a charge sufficient for the formation of A$_{1.0}$(MS$_2$) had passed. Nevertheless, there is no proof for any defined and stable phase with $x > 0.125$.

The CV of WS$_2$ reduction in KPF$_6$/DMSO is very similar to that for the reduction of MoS$_2$. The potential $E_{1/2}$ is, however, close to $-1.9$ V vs SCE, thus being 0.4 V more negative than that of the MoS$_2$ compound. This agrees with the observation that MoS$_2$ but not WS$_2$ is reduced in solutions of \textit{n}-butyl lithium in hydrocarbons.

In N(CH$_3$)$_3$Cl/DMSO there is no indication for a reduction of MoS$_2$. This result was surprising as the cathodic stability of N(CH$_3$)$_3$ should be sufficient for formation of MoS$_2$ intercalation compounds. Intercalates of graphite with N(CH$_3$)$_3$+ are readily formed at graphite cathodes in N(CH$_3$)$_3$Cl/DMSO.$^{10}$

Reduction of MoS$_2$ in solutions of alkali salts in 1,2-dimethoxyethane (DME) proceeds very similar to the reactions in A+/DMSO electrolytes. The potential/charge-curves are not characterized by a significant step but products A$_2$(DME)MoS$_2$ obtained after the theoretical charge transfer calcu-
latted for  \( x = 0.125 \) showed sharp X-ray reflections. Whereas the basal spacing of the \( \text{Li}^+ \) form with 14.49 Å is close to the spacing for the correspondent DMSO solvate, the spacings of the \( \text{Na}^+ \) and \( \text{K}^+ \) form amount to 15.5 Å resp. 14.98 Å and thus are considerably lower as compared to the \( \text{Na}^+ \) and \( \text{K}^+ \) compounds obtained in DMSO solutions (Table I). It is obvious, however, that solvent molecules have been taken up into the interlayer space in all cases. The ratio of the anodic:cathodic peak areas in CVs in KPF/\( \text{DME} \) was found to be smaller than that observed for KPF/\( \text{DMSO} \) electrolytes.

Conclusions

The results presented above clearly establish the existence of a defined stage \( A_{0.125(\text{solv})}^{\text{MoS}_2} \) in the reduction of \( \text{MoS}_2 \) in DMSO electrolytes; WS\(_2\) electrodes show basically similar reactions. No stable compounds were found beyond the ratio \( e^-:\text{MoS}_2 = 1:8 \) for these d\(^2\) metal chalcogenides. This is supposedly due to the differences in the electronic structure of these compounds as compared to the d\(^0\) and d\(^1\) metal dichalcogenides which are able to yield stable reduction products at considerably higher reduction stages under correspondent conditions.

Experimental

DMSO (analytical grade) was purified by refluxing at reduced pressure over CaH\(_2\) and subsequently fractionating in vacuum over a 1.5 m packed column. DME (reagent grade) was refluxed over Na and distilled at normal pressure. All solvents were saturated with purified Ar, solutes were vacuum-dried: NaBF\(_4\) and KPF\(_6\) at 180 °C for 20 h, LiClO\(_4\) at 180 °C for 40 h, RbI and CsI at 140 °C for 10 h and N(\( \text{CH}_3 \))Cl at 100 °C for 20 h.

Mo\(_2\) powder (chem. pure, 2 H-Mo\(_2\) modification) was pressed into Ni-gauze at 5000 kg · cm\(^{-2}\) and sandwiched between porous glass to avoid losses caused by exfoliation. All current densities correspond to the geometrical surface and can only be approximate values.

Potentials were measured vs the saturated aqueous calomel electrode (SCE) which was separated from the compartment of the working electrode by two fritted tubes filled with working electrolyte. The lower tube end terminated in a Luggin-capillary which was positioned close to the working electrode.

All measurements were carried out in cells of the double-H type, fitted with an inlet for inert gas. The working electrode was faced by two Pt-counter electrodes, separated by glass diaphragms. For cyclic voltammetry a Bank “Wenking” 68 FR 0.5 potentiostat, a Bank VSG 72 voltage scan generator and a Hewlett Packard 7004 B X/Y-recorder were used. Constant current was controlled by the potentiostat via a constant voltage decay at an external resistance. X/t-recorders with a high impedance operational amplifier Knick Diomod 73 W served for the continuous recording of potentials.

X-ray investigations were performed by powder methods in sealed glass capillaries with CuK\(_{\alpha}\) radiation. Precautions were taken to exclude moisture and oxygen on transfer of the sample material to the capillaries.

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