

Electrical & Catalytic Properties of Lithium Doped Molybdenum Trioxide

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Electrical conductivity and Seebeck coefficient of pure and lithium doped MoO_3 have been measured. MoO_3 has been found to be *n*-type but it changes to *p*-type when the lithium content is more than 0.7 mole%. This change has been ascribed to lithium entering the substitutional positions in the lattice. The ESR spectra of *n*-type samples show signal due to Mo^{5+} , but this is not observed in the *p*-type samples. Isopropyl alcohol undergoes dehydration predominantly and the catalytic activity first increases and then decreases with doping; the increase in activity coincides with the increase in *n*-type conduction and the decrease in activity with the change over to *p*-type conduction. In the presence of isopropyl alcohol vapours, conductivity of MoO_3 sharply increases whereas the *p*-type doped oxide shows a change in the type of the charge carriers. A relationship between the electrical conductivity and the catalytic activity has been established.

VARIOUS attempts have been made to relate the catalytic activity of semiconducting oxides to their electrical properties. Earlier results of Roginskii¹ and Wagner and Hauffe² have been explained on a more rigorous theoretical basis by Wolkenstein³. In order to study the effect of electrical properties on the catalytic activity of an extrinsic semiconductor, it is convenient to modify its electrical properties systematically by doping. Most of the work of this type has been done on 3d metal oxides⁴, particularly on ZnO and NiO and little has been reported on the 4d metal oxides even though quite a few of them are important catalysts. In this paper, we report the electrical and catalytic properties of molybdenum trioxide doped with lithium using decomposition of isopropyl alcohol (*i*-PrOH) as a model reaction since *i*-PrOH can undergo dehydrogenation and dehydration with equal ease, and is free from any appreciable side reaction⁴.

Materials and Methods

Pure molybdenum trioxide was obtained by heating ammonium paramolybdate (Baker analysed) at 400°. The doped samples were prepared by thoroughly mixing MoO_3 with the requisite quantities of Li_2CO_3 (AR) in an agate mortar in benzene medium. The dried samples were pelletized in a die at a pressure of 8 tons/sq inch, heated in a muffle furnace by gradually raising the temperature up to 400° and kept at this temperature for 24 hr. The bulk density of the sintered pellets was about 60 per cent of X-ray density. Pellets of 20 mm diameter and 4 and 10 mm thickness were used for the measurement of resistivity and Seebeck coefficient respectively. The pellets were crushed to powder for surface area measurement and catalytic studies.

Isopropyl alcohol (AR) was tested by vapour phase chromatography for purity before use.

Electrical properties—For the measurement of electrical resistivity a pellet was pressed between two circular platinum discs in a sample holder (Fig. 1a) and placed in the constant temperature zone of a tubular furnace. For the measurement of Seebeck coefficient (α) the two ends of the pellet were kept at a temperature gradient of about 10° by an auxiliary heater. The temperature of the

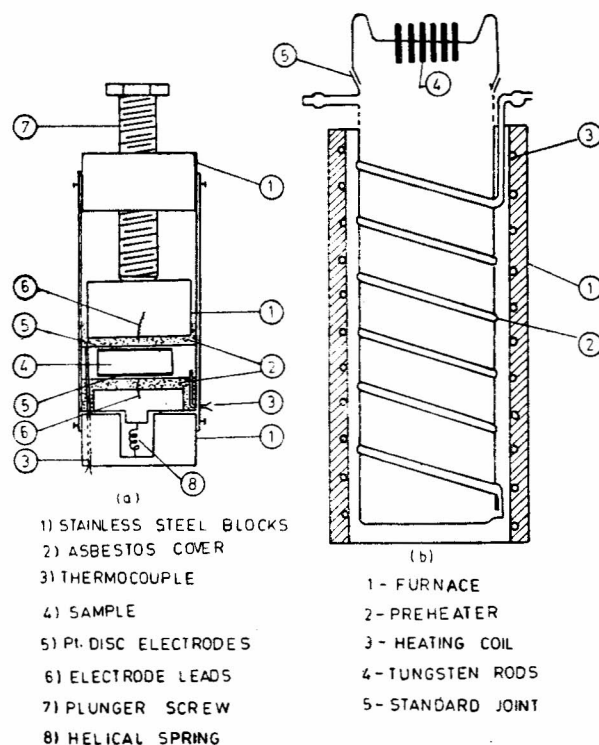


Fig. 1 — Arrangement for the measurement of electrical resistivity and Seebeck coefficient: (a) sample holder; (b) container

furnace was controlled to $\pm 2^\circ$ using a Philips plastomatic temperature controller. The sample was connected in series with a standard resistance and a d.c. power supply (12 V battery). The voltage drop across the sample and the standard resistance were read on a d.c. microvoltmeter (Philips PP 9004), from which the resistivity of the sample was obtained.

For measuring resistivity in different ambient atmospheres, the cell was placed in a glass tube fitted with ground glass joints (Fig. 1b). The electrical leads were taken out through sealed tungsten rods.

X-ray measurements — X-ray diffraction patterns were recorded on a Philips X-ray diffractometer (PW 1051) using Cu-K α radiation filtered through a nickel foil.

ESR spectra — ESR spectra were recorded on a varian V 4502 X-band spectrometer using diphenylpicrylhydrazyl (DPPH) as the standard.

Surface area — Surface areas of the samples were measured by the BET method using nitrogen adsorption at the boiling point of nitrogen using 10 g of the sample. All the samples were found to have low specific surface area, between 2-3 m²/g.

Catalytic activity — A conventional flow reactor was used. The powdered catalyst (1.5 g) was packed between glass wool plugs in a reactor tube with a thermocouple near the catalyst bed. The temperature was controlled to $\pm 1^\circ$. A steady supply of the reactant was maintained by an arrangement similar to that described by Griffith *et al.*⁵. Before each run, the catalyst was activated by passing air at 400° for 4 hr which was found to restore the original activity of the catalyst. The reaction was studied in the temperature range 200-350°.

The liquid products (*i*-PROH, water and acetone) were analysed by vapour phase chromatography on a AIMIL Mark II chromatograph using TCD detector and hydrogen carrier gas. The gaseous products contained only hydrogen and propylene.

Results and Discussion

The mixture of MoO₃ and Li₂CO₃ in the pelletized form on heating liberated equivalent amount of CO₂ and the lithium entered the lattice. Doped samples with 0.4, 0.7, 2 and 6 mole % of lithium were prepared. Log plots of conductivity (σ) versus reciprocal temperature are presented in Figs. 2 and 3. Activation energy of conduction (E) was evaluated from the plots. The variation of Seebeck coefficient (α) with temperature is shown in Fig. 4. MoO₃ is a *n*-type of semiconductor. By doping MoO₃ with 0.4% or more of Li⁺, σ increases and E decreases. With 0.7% of Li⁺, conductivity changes to *p*-type. These results are summarized in Table 1. X-ray diffraction patterns show that the only phase present in the samples containing up to 2% lithium is the MoO₃ phase. A new weak X-ray line in addition to those due to MoO₃ appears in the 6% doped sample.

The band gap in molybdenum trioxide has been reported to be 3.66 eV by Deb⁶ from conductivity measurements while Dickens and Nield have reported a value of 2.96 eV based on spectral studies⁷.

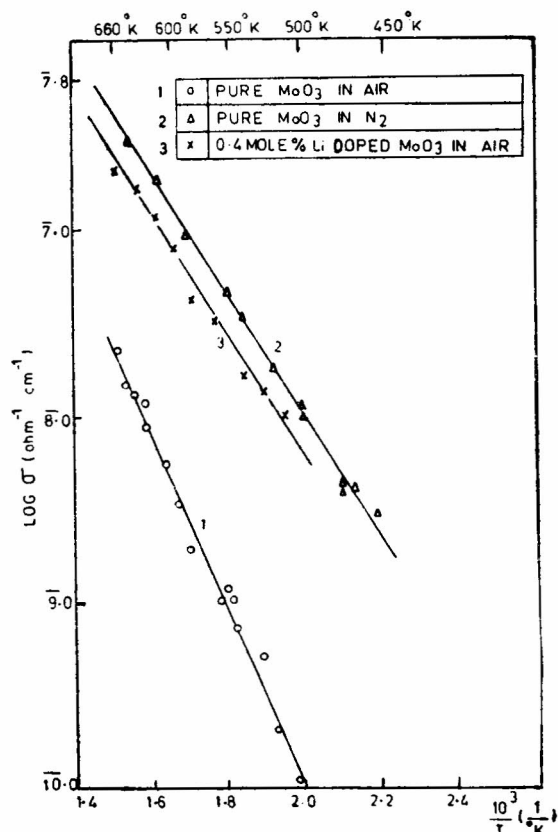
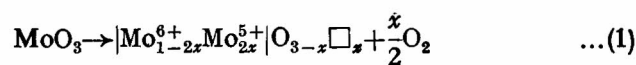


Fig. 2 — Plots of $\log \sigma$ versus $1/T$ for MoO₃ and 0.4 % lithium doped MoO₃

In either case, intrinsic conduction will be small in the temperature range of our studies, whereas extrinsic conduction will predominate. It is well known that molybdenum trioxide is oxygen deficient. The sample on heating may undergo some oxygen loss according to Eq. 1,



and form a composition which can be represented as MoO_{3-x}. This may facilitate a hopping conduction with electrons jumping from one molybdenum site (Mo⁵⁺) to another (Mo⁶⁺). This, however, does not seem likely as a hopping model would require α to be constant over a wide temperature range. Alternatively, Mo⁵⁺ may form an impurity level below the conduction band and conductivity may arise due to excitation of electrons from the impurity levels to the conduction band.

Two different descriptions are available for the energy diagram of MoO₃. According to Deb⁶, the valence band consists of oxygen 2*p* states and the conduction band represents the 4*d* band with some possible overlap with 5*s* band. Dickens and Nield⁷ have presented a molecular orbital description of a discrete MoO₃ unit according to which the highest filled level is *p* π^* non-bonding level and the next is the empty π^* level. In an extended lattice, these will broaden to form valence band and conduction band respectively. Both the models,

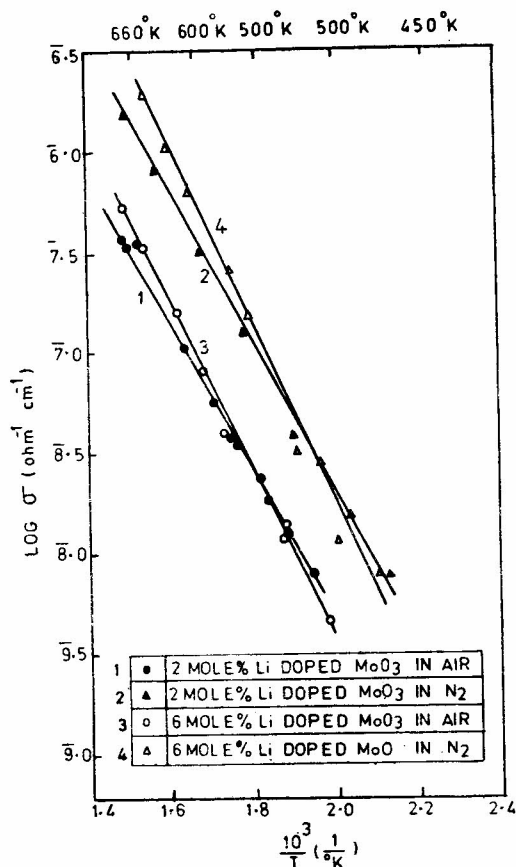
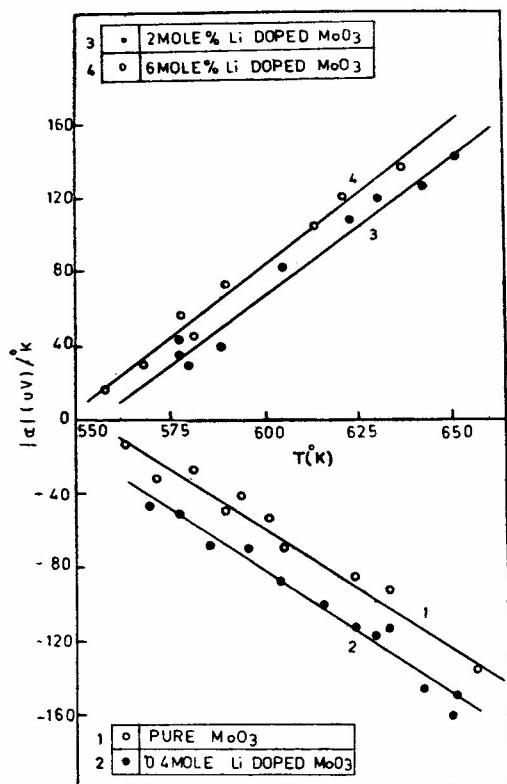

 Fig. 3 — Plots of $\log \sigma$ versus $1/T$ for the doped samples containing 2 and 6 mole% lithium


Fig. 4 — Plots of Seebeck coefficient versus temperature for the different samples

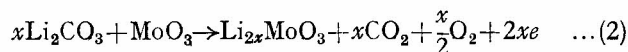
 TABLE 1 — ELECTRICAL PROPERTIES OF PURE AND DOPED MoO₃

Sample	E (eV)		Type of conduction (in air)
	In air	In nitrogen	
MoO ₃	0.96	0.69	<i>n</i> -Type
MoO ₃ +0.4% Li ⁺	0.64	—	do
MoO ₃ +0.7% Li ⁺	0.83	—	<i>p</i> -Type
MoO ₃ +2.0% Li ⁺	0.74	0.74	do
MoO ₃ +6.0% Li ⁺	0.84	0.88	do

however, are speculative and not based on rigorous theoretical work.

Conductivity has been found to be much higher in nitrogen atmosphere than in air. This is because of greater deviation from stoichiometry at low oxygen partial pressure. If after removal of nitrogen the sample is heated in air, it shows same conductivity as measured originally in air.

Doped molybdenum trioxide— The increase in electrical conductivity (σ) by adding 0.4 mole% lithium may be explained as due to interstitial Li⁺ according to the reaction (Eq. 2):



These liberated electrons will create shallow donor levels and thus increase electronic conduction. At higher concentration (0.7% and more), Li⁺ possibly enters the lattice substitutionally. This is possible as Li⁺ has ionic radius (0.62 Å) comparable to that of Mo⁶⁺ (0.68 Å). ESR studies of copper doped MoO₃ single crystals by Ioffe *et al.*⁸ have shown that Cu⁺ ions occupy both, interstitial as well as substitutional positions. On entering the lattice, substitutional Li⁺ will create new cationic and equivalent number of anionic lattice sites, thus creating a charge imbalance in the lattice. This will initially oxidize all Mo⁵⁺ to Mo⁶⁺ and then create oxide ion vacancies which are equivalent to positive holes⁹. This will amount to the acceptor level giving rise to *p*-type conduction. If this is the case, the *p*-type sample should not show the ESR signal due to Mo⁵⁺. The ESR spectrum of MoO₃ shows a signal due to Mo⁵⁺ ($g = 1.975$) which is absent in the spectrum of 6% doped sample as expected.

Catalytic activity— The predominant reaction on all the catalysts was found to be dehydration of *i*-PrOH to propylene. In the case of pure MoO₃, no dehydrogenation was observed below 268° at which temperature about 14% of acetone was formed, but this too decreased with further increase in temperature. In the case of the catalyst with 0.4% Li⁺, some diisopropyl ether (DIE) was found in the product (vp to 0.4%). Catalysts with 2 and 6% Li⁺ were free from any side reactions. The results are summarized in Table 2 for two different contact times. It is clear that dehydration activity increases up to 0.4% of Li⁺ and then falls with further increase in lithium content.

It is generally believed that dehydration of alcohol takes place at the Bronsted or Lewis acid centres on the surface¹⁰⁻¹². Addition of Na⁺ and K⁺ has been found to reduce alcohol dehydration

TABLE 2 — DEHYDRATION OF *i*-PrOH ON VARIOUS CATALYSTS AT DIFFERENT TEMPERATURES

(Amount of catalyst used: 1.5 g)

Catalyst	Surface area (m ² /g)	Temp. (°C)	H ₂ O formed (mole/100 mole of <i>i</i> -PrOH)	
			A	B
MoO ₃	2.91	218	17.5	25
		248	27.0	35
		293	55.0	85
		337	76.0	—
MoO ₃ +0.4% Li ⁺	2.7	221	14.0	27
		250	40.0	55
		280	52.0	—
		337	92.0	—
MoO ₃ +2.0% Li ⁺	2.3	248	11.2	23
		293	23.5	48
		337	48.0	72
		—	—	—
MoO ₃ +6.0% Li ⁺	2.0	248	5.0	10
		293	18.0	34
		337	20.0	36
		—	—	—

A = contact time 0.2 sec; B = contact time 0.4 sec.

on alumina. According to this view, the catalyst with 0.4% of Li⁺ should be less active in dehydration than pure MoO₃. The presence of Lewis acid centres may be responsible for dehydration, but there does not appear to be much evidence that addition of alkali metal can increase Lewis acidity. Alternatively, one can use the electronic theory of catalysis to explain these changes in activity. The addition of impurity modifies the electrical properties of a semiconductor in different ways depending upon whether the impurity goes to an interstitial or a substitutional position.

We have observed in the case of MoO₃ that an increase in the *n*-type conductivity increases dehydration and as soon as the oxide becomes *p*-type, activity drastically falls. Thus, dehydration of *i*-PrOH on these catalysts is an acceptor or *n*-type reaction according to Wolkenstein's nomenclature¹³ — the reaction is favoured by an increase in electron concentration.

In order to find out how the electrical properties of catalysts change during the reaction, we measured the conductivity of the pellets in *i*-PrOH vapour (*p*_{*i*-PrOH} = 0.2 atmosphere) diluted with nitrogen. The results are shown in Fig. 5. For pure MoO₃, σ increases rapidly with time. For the *p*-type samples, σ falls initially and then increases and at this point of change conduction changes to *n*-type. These results show that the Fermi level rises during the reaction.

It has been pointed out¹⁴ that adsorption of an alcohol molecule is accompanied by the donation of electrons to the surface. The rapid rise of σ on introducing *i*-PrOH seems to indicate that the alcohol adsorption is a fast process. It has also been reported that chemisorption of alcohol on both, *n*-type and *p*-type oxides is nonactivated¹⁵. All these facts indicate that adsorption of alcohol may not be the rate determining step.

TABLE 3 — EFFECT OF WATER VAPOUR ON DEHYDRATION OF *i*-PrOH*

Temp. (°C)	Partial pressure (atmosphere)		Conversion (%)
	Alcohol	Water	
CATALYST MoO ₃ ; CONTACT TIME 0.2 SEC			
250	0.75	—	26.5
	0.67	0.08	10.5
	0.54	0.21	5.6
CATALYST MoO ₃ +6% Li ⁺ ; CONTACT TIME 0.2 SEC			
250	0.75	—	1.45
	0.54	0.20	12.4
CATALYST MoO ₃ +6% Li ⁺ ; CONTACT TIME 0.25 SEC			
350	0.75	—	18.1
	0.67	0.08	17.0

*Partial pressure of N₂ was 0.25 atmosphere in all the cases.

In order to decide whether the rate determining step is the surface reaction or the desorption of the products, we studied the dehydration activity of the catalysts in the presence of water vapour. The results are presented in Table 3. The presence of water vapour drastically lowers the activity of MoO₃. This, according to Krylov's rate expression¹⁶ should mean that desorption of water is the rate determining step. However, water has very little effect on dehydration for the 6% doped catalyst.

If we accept the desorption of water as the rate determining step, the change in dehydration activity with doping can be interpreted in terms of the electronic theory of Wolkenstein¹³. Desorption of water

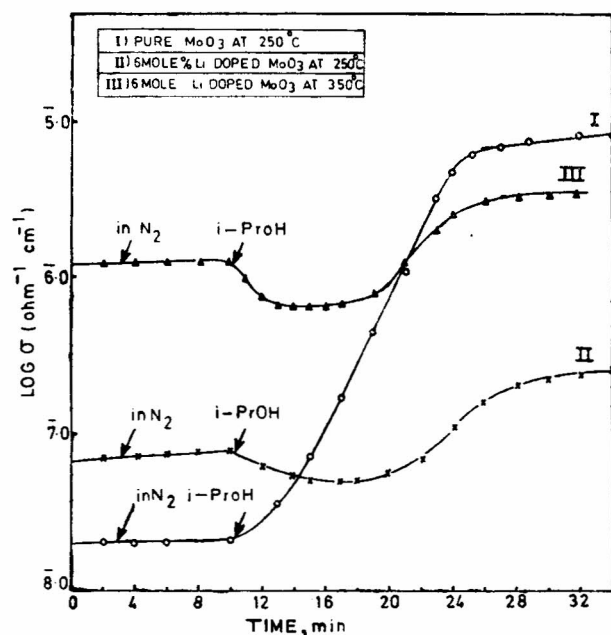


Fig. 5 — Variation of conductivity with time in *i*-PrOH vapour for the different samples

will be favoured by a *n*-type material as water on desorption will remove electrons from the surface. This will be more difficult on a *p*-type semiconductor. However, under the reaction conditions, even the catalyst containing 6% lithium becomes *n*-type, with the difference that its conductivity is much lower than that of MoO₃ under similar conditions, thus indicating lesser availability of electrons necessary for water desorption. This may be the reason for decrease in catalytic dehydration. On the other hand, catalytic dehydrogenation which is normally expected on a *p*-type semiconductor is not observed, because it is no longer *p*-type under the reaction conditions. At the same time, desorption of water has already become difficult so that the presence of water vapour in the reactant has little effect on dehydration.

It is interesting to note that the 0.4% doped sample has higher activity than pure MoO₃ only at sufficiently high temperature (248° and above, Table 2). MoO₃ is a poor conductor and its semiconducting property becomes significant above 250°. In V₂O₅ (a much better conductor), on the other hand, the increase in catalytic activity by doping with Li⁺ is observed at much lower temperature¹⁷.

Thus, the catalytic dehydration of *i*-PrOH on semiconducting oxides can be explained in terms of the semiconductor properties of the latter. This has been shown more clearly in the case of the lithium doped vanadium pentoxide catalysts, in which case both catalytic activity and *n*-type conductivity has been found to increase with

increased doping¹⁷. Studying the effect of electric field on the dehydration of *i*-PrOH on a rutile film, Keier *et al.*¹⁸ have arrived at similar conclusions.

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