Electrointercalation in Transition-metal Disulphides

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Summary Metals and other electron donors like ammonia can be electrochemically intercalated into layered transition-metal disulphides at 25° from aqueous and organic solutions of their salts.

THE disulphides of group IVB and VB transition metals have layered structures, the layers comprising metal atoms sandwiched between hexagonally close-packed sulphur sheets. The bonding between these layers is very weak and a large number of metals and other electron-donating species can be inserted between the layers giving intercalation compounds.[1]

We now report a new technique, in which intercalation is performed electrochemically. The layered material serves as the cathode of an electrolytic cell, in which the electrolyte is an aqueous or organic solution of a salt of the species to be intercalated, *e.g.* NH_4I in acetone, $CuSO_4$ in water.

Ag_xTaS_2 was prepared by dipping a silver wire electrode and a TaS_2 crystal attached to a platinum wire electrode into an aqueous silver nitrate solution. On connecting the two wires together a current flowed, due to the silver concentration gradient, and silver ions were discharged into the TaS_2 crystal. The lattice spacing of the crystal increased from 6·04 Å for pure TaS_2 to 6·85 Å at x *ca.* 0·2 and 7·21 Å at x *ca.* 0·6. The copper analogue was prepared similarly using a copper anode and an aqueous copper sulphate electrolyte; the lattice expanded to 6·56 Å for x *ca.* 0·6. This is in very good agreement with the value 6·57 Å found by DiSalvo *et al.*[2] for $Cu_{2/3}TaS_2$ prepared by heating TaS_2 and copper powder at 1025° for several days. Similar compounds are formed with TiS_2 and $NbSe_2$.

For the intercalation of ammonia a solution of ammonium iodide in acetone served as the electrolyte and Pt or Au as the anode. On electrolytic decomposition (*ca.* 2 V across the electrodes) ammonium ions discharged at the sulphide surface, ammonia intercalated the crystal lattices and hydrogen was evolved. The compound formed, $NH_3 \cdot TaS_2$, had the same physical and structural properties as samples prepared by reaction of TaS_2 with liquid ammonia. An expansion of the lattice parameter of 3 Å was found for TiS_2, $TiSe_2$, ZrS_2, TaS_2, and $NbSe_2$. Pyridine was intercalated in an hour by decomposition of a methanol solution of pyridinium hydrochloride; hydrogen was again evolved at the cathode on intercalation. The TaS_2 lattice expanded to 11·87 Å, the same as samples formed by heating the sulphide and pyridine in sealed ampoules at 200° for a day.[1] Trimethylamine was intercalated into TaS_2 on decomposition of a solution of trimethyl ammonium chloride, giving a previously unreported compound of lattice parameter 9·63 Å.

It was found possible by electrolytic decomposition of 0·1N aqueous HCl to form H_xTaS_2 for $x = 0$—0·15. The structure of this phase is complex, the lattice expanding to *ca.* 50 Å and then decomposing *via* a number of other phases, back to that of TaS_2, contrary to a recent report.[3] An enhanced superconducting transition temperature observed on intercalation, 0·8 K to 3 K was however retained.[4] The hydrated intercalates of the alkali metals were formed by electrolysis of their chloride solutions. These materials were similar to those formed on reaction of the sulphides with hydroxide solutions.

The electrointercalation technique can be used at normal temperatures, minimizing thermal decomposition of the reactants or products and allowing the preparation of intercalation compounds unstable at elevated temperatures such as the layered Cu_xTiS_2.

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[1] F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. DiSalvo, and T. H. Geballe, *Science*, 1971, **174**, 493.

[2] F. J. DiSalvo, G. W. Hull, Jun., L. H. Schwarts, J. M. Voorhoeve, and J. V. Waszczak, *J. Chem. Phys.*, 1973, **59**, 1922.

[3] S. F. Meyer, R. E. Howard, G. R. Stewart, T. H. Geballe, J. V. Acrivos, F. J. DiSalvo, and D. W. Murphy, *Bull. Amer. Phys.Soc.*, 1974, **19**, 76.

[4] A. H. Thompson, unpublished work.