ELECTROSYNTHESIS OF COPPER-COPPER(I) OXIDE-A BLACK COMPOSITE POWDER

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Several electrosynthetic routes have been reported for both Copper and Copper (1) oxide [1]. There is hardly any mention of a synthetic route in a nonaqueous medium for a Comporite Powder ($Cu-Cu_2O$). This communication reports the preparation of a componite powder of $Cu-Cu_2O$ (nearly 1:1 in comparition) by cathodic deposition in aceto nitrile medium.

EXPERIMENTAL

A stainless steel cathode (1cm x 2cm x 0.2cm) and a copper anode (1 cm x 1 cm x 0.4 cm) are suspended one cm apart in an electrolysis glass versel containing 150 ml of acetomitule (BDH, undistilled) in which 500-600 mg of pysidinumum hexafluero phosphate $2(C_5H_5NH^+PF_6^-)$ as the supporting electrolyte has been dissolved. A DC Voltage [Ac/Dc rectifier] of 4.2 volts is impressed for 1 hour. A silver coulometer in series registers the amount of current. It is observed that after a lapse of about five, minutes, a black deposit appears on the cathode. This increases with time and as it is loosely held, falls away when stirred. At the end of the experiment the deposit is filtered off and washed with ether and dried in an air oven (105°C) for 10 minutes and weighed. In a typical case, the amount of deposit obtained is 46.7 mg. Analysis indicates a copper content of 90.8% and the X-ray powder diffraction data confirms the presence of elemental copper and copper(1) oxide only. From the current data, the calculated value of 'n' is 0.98 indicative of a one electron transfer process. The copper anode has in parts a fine white deposit which on analysis and ir spectral data, reading showns it to be copper hexafluoro phosphate. (Cu(i) PF_6). The electrolyte is evaparated under vacuum and a white deposit is left behind. The deposit is analysed for its copper, pyridine and PF_6^- contants by stan ard methods. An ir spectrum is recorded, inbedded in a KBr pellet on a Pakin Elmer 588, ir spectrometer. From this, the white deposit is analysed to be tetrakis (acetonitrile) copper(I) hexafluro-phosphate $[Cu^+(CH_3CN)_4]\ PF_6^-$. Such a complex has been previously prepared by a wet chemical of method [3].

RESULTS AND DISCUSSION

The results indicate that copper dissolves annodically and forms the complex salt, tetrakis (aceetonitrile) copper (1) hexafluoro phosphate. This complex salt is soluble in acetonitrile and gives of the Cu^+ ion at the cathode to form finely divided elemental copper, which partially undergoes oxidation by the oxygen/water ($\sim$ 0.2%) present in the actonitrile to form Cu(1) oxide. Alternatively, two complexes could be formed in the solution, $[Cu^+(CH_3CN)_4]\ PF_6^-$ and $[Cu^+(CH_3CN)_4]\ OH^-$. These undergo decomposition at the cathode simultaneously to form a fine composite of copper and copper(1) oxide. The X-ray data and analysis supports the presence of both in nearly 1:1 composition. This composite deposit is deep brown black and free flowing on drying but as a cathodic deposit it appears spongy. If the electrolysis is continued for more than one hour, the moisture content in acetonitrile drops due to electrolysis of water ie. forming hydrogen and hydroxyl ion. The hydroxyl ion being consummed as $Cu^+(CH_3CN)_4\ OH^-$ and later undergoing cathodic conversion to Cu_2O and hydrogen. The copper now in solution as $[Cu(CH_3CN)_4]\ PF_6$ undergoes cathodic reduction to bright copper and there is a continuous anodic dissolution of copper and a cathodic deposition of pure bright copper powder which, being non adherent on stainless steel drops off. By maintaining 0.2% to 0.5% by weight of water in accetonitrile, a black composite deposit of copper and copper (I) oxide may be obtained. The formation of cuprous hexafluro phosphate on the anode is due to chemical precipitation of the formed Cu^+ ion and the hexafluro phospharate available in solution. This undergoes complexation with acetonitrile and gets dissolved as $[Cu(CH_3CN)_4]\ PF_6$. It is of interest to mention that both the pyridinuim ion and hexaflurophosphate ion do not undergo any electrochemical oxidation or reduction under these conditions.

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REFERENCES

1. "Electrochemical Synthesis of Inorganic *Compounds*". A Bibliography-Zottan Nagy (Ed) (Plenum Press New York) (1985) 97p and 305p

2. K.Syed Mohamed, D.K. Padma, R.K.Kalbandkeri and A.R. Vasudeva Murthy, *J. Fluorine Chem.* **23**, (1983) 509.

3. G.J. Kubas, *"Inorganic Synthesis"*. (John wiley and Sons) N.Y. 1979. **19**, 90p.