

Reactions of Copper in Molten Alkali-Metal Nitrite

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Abstract

When molten NaNO_2 is electrolysed between copper electrodes, a yellow precipitate which contains copper(I) forms at the cathode.

It seems probable that a cuprite with the empirical formula $\text{Na}_2\text{O}, \text{Cu}_2\text{O}, \text{H}_2\text{O}$ is initially formed and is then slowly oxidized either by species present in the melt or by air. If sufficient Na_2O_2 is added to saturate the melt (i.e., solid Na_2O_2 is present), the precipitate partly dissolves to form an orange-red solution which forms a green solid on freezing. This may contain a copper(II) or copper(III) cuprate.

We have recently described¹⁻³ the production of Fe^{V} , Mn^{V} and Co^{V} when molten sodium nitrite is electrolysed between appropriate electrodes or when metallic salts are added to solutions of Na_2O_2 in this melt. During the present experiments we compared the behaviour of these metals with that of copper under the same conditions.

When copper electrodes are used¹ to electrolyse molten NaNO_2 , rapid cathode attack is followed by the formation of an intensely yellow precipitate which gradually darkens and finally becomes dark brown on standing in the light. This deep brown precipitate appears stable, although some black CuO is occasionally observed at the melt-air interface. The yellow precipitate is stabilized if moist nitrogen is passed through the melt but decomposes rapidly if the melt is thoroughly dried by evacuation before the experiments. The yellow or yellow-brown precipitate immediately dehydrates to red Cu_2O if added to cold concentrated H_2SO_4 .

Two separate products obtained from the melt by extraction gave analyses closely corresponding to whole number ratios of components. The first of these was obtained by extraction with dry dimethyl sulphoxide. Two-thirds of the copper was found to be present as Cu^{I} by standard titrimetric procedures. On standing the percentage of Cu^{II} increases. The analysis of this product was Na, 24.5 ± 1 ; Cu, 49.2 ± 1.5 ; H (as H_2O), $0.6 \pm 0.5\%$, which corresponds closely to the empirical formula $2\text{Na}_2\text{O}, \text{Cu}^{\text{I}}_2\text{O}, \text{H}_2\text{O}, \text{Cu}^{\text{II}}\text{O}$ (required Na, 25.2; Cu, 52.2; H as H_2O , 0.6%). Sample 2, extracted from the melt with water, was a dark-brown solid. It contained no alkali-metal oxide and only a small proportion of Cu^{I} , which oxidized in air (Found: Cu, 79.8 ± 0.4 ; H, 0.4 ± 0.3 . Required for $\text{Cu}^{\text{I}}_2\text{O}, \text{H}_2\text{O}, 4\text{Cu}^{\text{II}}\text{O}$: Cu, 79.6; H, 0.4%).

¹ Temple, R. B., and Thickett, G. W., *Aust. J. Chem.*, 1972, **25**, 655.

² Temple, R. B., and Thickett, G. W., *Aust. J. Chem.*, 1973, **26**, 1137.

³ Temple, R. B., and Thickett, G. W., *Aust. J. Chem.*, 1973, **26**, 2051.

$\text{Cu}_2\text{O}\cdot\text{H}_2\text{O}$ is a yellow precipitate well documented in the literature.⁴ Although it is sometimes formulated as CuOH , X-ray analysis has indicated that the H_2O is probably not chemically bound.^{5a} It therefore seems probable that Cu^{I} oxide is initially formed at the cathode.

It is possible that this may then form a cuprite of empirical formula $\text{Na}_2\text{O}\cdot\text{Cu}_2\text{O}\cdot\text{H}_2\text{O}$, which is slowly oxidized either by species present in the melt or by exposure to air. We cannot be certain from our results that the yellow-brown substance formed is not merely a mixture of oxides but the fact that it forms in the melt even under vacuum seems to indicate that both the melt and the product contain traces of very strongly bound water.

Copper metal, $\text{Cu}^{\text{II}}\text{O}$ or $\text{Cu}_2^{\text{I}}\text{O}$ all react immediately with solutions of Na_2O_2 in the melt to form a red-orange solution from which a yellow precipitate forms on standing. This redissolves, if more Na_2O_2 is added, to re-form the deep orange-red solution, which is stabilized by evacuating the apparatus. The orange-red melt freezes to form a green solid, this colour change being reversible and the intensity of the green colour depending on the amount of Na_2O_2 added.

The nature of this soluble copper species which changes from red in the melt to green in the solid is not certain. Having regard to our observations with other metals reported previously^{1,2} it seems probable that it is a cuprite or cuprate i.e., that it contains $(\text{CuO}_x)^{y-2x}$ with x and $y = 1, 2$ or 3 , with Cu^{I} , Cu^{II} or Cu^{III} .

Eluard and Tremillon have studied the dissolution and reactions of copper oxides in molten hydroxides.⁶ According to them, CuO^- and CuO_2^{3-} (red Cu^{I} ions) appear to be formed when O_2^{2-} reacts with copper in these melts. Higher oxidation species such as cuprates ($\text{Cu}^{\text{II}}\text{O}_2^{2-}$) do not seem to form, and this suggests cuprites are more stable.

These workers also observed that $\text{Cu}^{\text{I}}\text{O}$ dissolved in so-called 'basic' hydroxide melts to form a red cuprite, oxide present in the solvent being simultaneously oxidized to peroxide. CuO was soluble to a certain limit, at which point $\text{Cu}^{\text{II}}\text{O}$ and $\text{Cu}^{\text{I}}\text{O}_2^{3-}$ coexisted.

Our present experiments in molten nitrite show strong parallels with the hydroxide results. We found that large additions of peroxide were necessary to keep the copper in solution. From this we may deduce that during electrolysis the bulk concentration of O_2^{2-} remains too low to retain copper in solution. The yellow precipitate therefore does not dissolve.

When solution does occur it is uncertain whether oxidation takes place or not. As the frozen melt is green, an oxidation state of copper higher than Cu^{I} appears to be present. Unfortunately magnetic measurements were inconclusive on this point. The frozen solutions appeared to be diamagnetic but this could be the result of too little copper complex in solution.

It is well known that magnetic measurements on copper are difficult to interpret because some Cu^{II} salts are only very weakly paramagnetic. Even $\text{Cu}^{\text{III}}\text{O}_2$ is diamagnetic,^{5b} which indicates a cancelling of the moments of the individual atoms because of their relative orientations whereas other considerations would lead us to

⁴ Emel'yanko, G. A., *Zh. Fiz. Khim.*, 1958, **32**, 2119.

⁵ 'Gmelins Handbuch der anorganischen Chemie' Copper, Part B, Syst. No. 60 (a) Suppl. 1, 1958, p. 97; (b) Suppl. 3, 1965, p. 1408 (Verlag Chemie: Weinheim).

⁶ Eluard, A., and Tremillon, B., *Z. Elektroanal. Chem.*, 1968, **18**, 277.

expect that this compound would be strongly paramagnetic. E.s.r. measurements might be able to throw some light on the nature of the green copper species in the solid.

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