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# MEMBRANE SEPARATION AND CONCENTRATION OF COPPER ION BY AN ION PUMP DRIVEN BY LIGHT

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A novel device for copper separation and concentration is presented in which light energy was used as driving potential. This was achieved by combining a photo-induced redox reaction to a redox potential-driven, carrier-mediated transport of copper ion through a polymer-supported liquid membrane.

Solvent extraction of metals is offering a versatile method for hydrometallurgy and waste-water treatment processes. A liquid membrane technique, a modified version of the separation technique by conventional solvent extraction is gaining attention as a possible alternative in the future for selective separation and concentration of metals from dilute aqueous solutions.[1,2] The driving energy for the membrane separation is usually supplied by a pH gradient or more generally an ion concentration gradient across the membrane, but any chemical potential may be applied to drive the process.

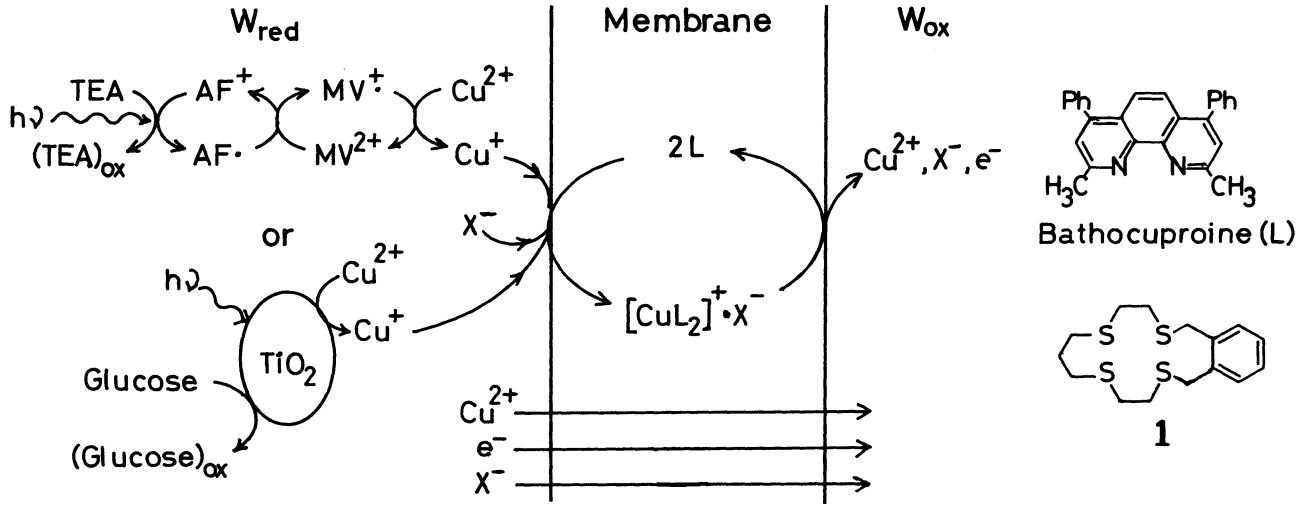


Fig. 1. Mechanism of light-driven copper transport through liquid membrane. $[CuL_2]^+ \cdot X^-$ represents the ion-pair association complex of copper with Bathocuproine (L) and an appropriate anion $X^-$. In the case of thiacrown **1** (Tc), $[CuTc]^+ \cdot X^-$ complex is formed. TEA, triethanolamine; $AF^+$ and AF·, acriflavine and its reduced form; $MV^{2+}$ and $MV^+ \cdot$, methyl viologen (1,1'-dimethyl-4,4'-bipyridinium) and its reduced form.

Table 1. Light-driven copper transport through a liquid membrane[a)]

| Run | Carrier[b)] | Reductant[c)] | Sensitizer[d)] (Electron mediator) | Lamp[e)] | Initial rate of transport (μM/h) |
|---|---|---|---|---|---|
| 1 | Bc | TEA | $AF^+$, ($MV^{2+}$) | Hg (L-42) | 20 |
| 2 | Bc | TEA | ($MV^{2+}$) | Hg (L-42) | 2.8 |
| 3 | Bc | TEA | $AF^+$, ($MV^{2+}$) | dark | 1.0 |
| 4 | Bc | TEA | $Ru(bpy)_3^{2+}$, ($MV^{2+}$) | Hg (L-42) | 12 |
| 5 | Bc | Glucose | $TiO_2$ | Xe | 8.7 |
| 6 | Bc | Glucose | none | Xe | 3.2 |
| 7 | Bc | Glucose | $TiO_2$ | dark | 3.7 |
| 8 | Bc | Glucose | $TiO_2$[f)] | Xe | 7.2 |
| 9 | Bc | $(NH_3OH)_2SO_4$ | none | dark | 57 |
| 10 | Tc | TEA | $AF^+$, ($MV^{2+}$) | Hg (L-42) | 7.0 |
| 11 | Tc | Glucose | $TiO_2$ | Hg | 6.3 |
| 12 | Tc | Glucose | $TiO_2$ | dark | 1.0 |
| 13 | Tc | $(NH_3OH)_2SO_4$ | none | dark | 42 |

a) Conditions. Runs 1∿9: $W_{red}$ contained 0.1 mM (1 M = 1 mol/dm$^3$) $Cu(NO_3)_2$, 10 mM KCl, and 0.5 M $CH_3CO_2NH_4$, while $W_{ox}$ contained 0.5 M $CH_3CO_2NH_4$ (air-saturated). Runs 10∿13: $W_{red}$ contained 0.1 mM $Cu(NO_3)_2$, 10 mM $NaPF_6$, and 0.1 M $CH_3CO_2NH_4$, while $W_{ox}$ contained 4 mM $Ce(SO_4)_2$ and 3 % $H_2SO_4$. b) 10 mM Bathocuproine (Bc) or 100 mM thiacrown **1** (Tc) in the membrane solvent. c) 10 mM TEA, 10 mM glucose, or 5 mM $(NH_3OH)_2SO_4$ was added in $W_{red}$ phase. d) 0.05 mM $AF^+$ (chloride), 0.05 mM tris-(2,2'-bipyridine)ruthenium(II) dichloride, 0.25 mM $MV^{2+}$ (dichloride), or 100 mg $TiO_2$ was added in $W_{red}$ phase as indicated. e) Hg, 500 W high-pressure mercury lamp; Xe, 500 W xenon lamp; L-42, 420 nm cut-off filter. f) Rutile type $TiO_2$; the others were anatase type.

In our previous works,[3,4)] the redox potential-driven copper transport through a liquid membrane was achieved by using Bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) as a carrier. A subsequent study indicated that a thiacrown compound **1** (13,14-benzo-1,4,8,11-tetrathiacyclopentadecane)[5)] could also be used for the same purpose. Copper ion was selectively transferred against its concentration gradient (active transport) between the two aqueous solutions separated by a polymer-supported liquid membrane. Now, the redox potential was

generated photo-chemically by using a sensitizing dye[6] or semiconductor suspension[7], and the system was coupled with the carrier-mediated copper transport (Fig. 1).

The apparatus used was the same as that described.[8] The cell was consisted of two compartments, $W_{red}$ and $W_{ox}$ (each 150 mL capacity), which were separated by a liquid membrane supported on a microporous polypropylene film (Duragard 2500, Polyplastics Ltd.). The effective membrane area was 28 $cm^2$. A diphenyl ether solution containing a carrier compound (*ca.* 0.04 mL) was applied to the film. $W_{red}$ phase (reducing aqueous phase) contained a photo-sensitizer system and was irradiated by an appropriate light source, while $W_{ox}$ phase (oxidizing aqueous phase) contained an oxidizing agent (air). The aqueous solutions were stirred at 30°C, and the aliquots of the solutions were taken periodically and analyzed.

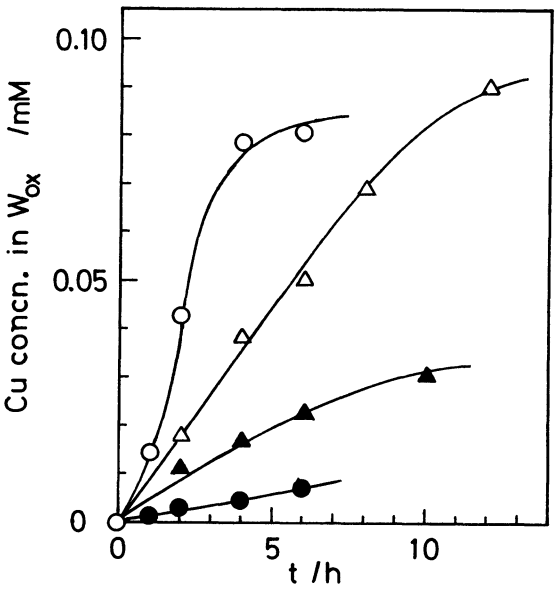


Fig. 2. Change in the copper concentration in $W_{ox}$ phase against time under the conditions in Table 1. ○, run 1; ●, run 3; △, run 5; ▲, run 7.

The results obtained are summarized in Table 1 and Fig. 2. Figure 2 shows the change in the concentration of copper ion in $W_{ox}$ phase against time when Bathocuproine is used as a carrier. The photo-system, triethanolamine - acriflavine - methyl viologen ($AF^+$ system) in $W_{red}$ phase produced blue cation radical of methyl viologen ($MV^{+\cdot}$) upon irradiation and resulted in the active transport of copper ion through the membrane.[9] When a titanium oxide suspension in $W_{red}$ phase was irradiated in the presence of a reducing agent such as glucose ($TiO_2$ system), the active transport of copper ion was similarly attained. Control experiments for $AF^+$ system (without acriflavine, run 2; in dark, run 3) and $TiO_2$ system (without $TiO_2$, run 6; in dark, run 7) indicated that the transport rates were considerably decreased in comparison with those of the complete systems (runs 1 and 5). The transport of copper in the control experiments is partly due to the production of reducing species by the reaction other than the normal photoreaction and partly due to the fact that copper is capable of transferring through the membrane in the divalent state ($Cu^{II}$-route).[3,4] The presence of triethanolamine blocked $Cu^{II}$-route because copper(II) was complexed strongly with the amine in the reducing phase (runs 3 and 7). The use of ruthenium complex as a sensitizer instead of acriflavine lowered the transport rate (run 4).

Copper ion was found to be adsorbed on the $TiO_2$ suspension, and this seemed to explain the lower rate of copper transport as compared with $AF^+$ system (runs 1 and 5). The adhesion of $TiO_2$ powder on the membrane surface[3] was another cause of the rate depression, but the effect was diminished by selecting proper stirring

conditions. Anatase type $TiO_2$ was more effective than the rutile type (runs 5 and 8).

Thiacrown **1** proved superior as a carrier to Bathocuproine with regard to the selectivity to copper among other metals (zinc, cadmium, *etc.*). This is because the thiacrown carrier does not extract the divalent metal into the membrane phase (absence of $M^{II}$-route). Both photo-systems, $AF^+$ system and $TiO_2$ system, were able to assist the thiacrown **1**-mediated copper transport (runs 10 and 11).

The efficiency of the light-driven processes as measured by the rate of copper transport or by the degree of final copper concentration varied according to the solution compositions as well as to the irradiation conditions. Generally, the rates were lower for the light-driven processes than for the hydroxylamine-driven-processes (runs 9 and 13), but the degree of final copper concentration was in the same range of magnitude ($\geq$80 % in $W_{ox}$ phase) for the both processes.

There is an increasing interest in the photo-induced electron transport or proton transport in bio- or synthetic membranes,[10-12] but few emphasized its potential for use in separation of metals. The application of light energy to a carrier-mediated transport process provides a new possibility for the separation and concentration of metals. The present light-driven copper concentration is yet far from practical use, but this principle is hopefully extended to other metals and eventually would make it possible to use solar energy for the chemical separation of specific metals.

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