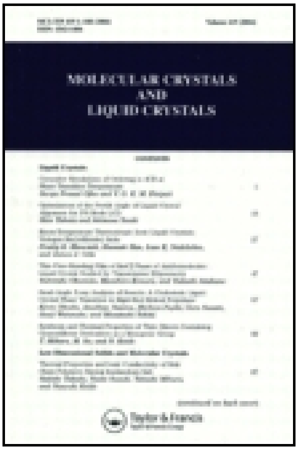

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electrochemical Behaviour of Copper Chloride GIC

Peter Scharff [a] & Rainer Opitz [a]

[a] Institut für Anorganische Chemie, TU Clausthal, Paul-Ernst-Str. 4, D-3392, Clausthal-Zellerfeld, Germany

Version of record first published: 23 Oct 2006.

To cite this article: Peter Scharff & Rainer Opitz (1994): Electrochemical Behaviour of Copper Chloride GIC, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 197-202

To link to this article: http://dx.doi.org/10.1080/10587259408050104

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 197–202
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

ELECTROCHEMICAL BEHAVIOUR OF COPPER CHLORIDE GIC

PETER SCHARFF AND RAINER OPITZ
Institut für Anorganische Chemie, TU Clausthal, Paul-Ernst-Str. 4, D-3392 Clausthal-Zellerfeld, Germany

Abstract Copper chloride GICs were investigated by means of cyclovoltammetric, pulsed galvanostatic and AC impedance measurements. It was found that the electrochemical reduction takes place in two different potential regions. A small amount of Cu(II) species is reduced to metallic copper via a Cu(I) intermediate. The majority is reduced in a two-electron-transfer-step at lower potentials. The deintercalation reaction is irreversible.

INTRODUCTION

Nowadays many primary lithium batteries are produced, however there is a need for new rechargeable lithium batteries. Perhaps a new system may work with intercalation cathodes. Intercalation electrodes have promising properties: good ionic and electronic conductivity at room temperature, almost constant volume during discharge, high energy density. It was often proposed to use graphite intercalation compounds (GICs) as cathode materials. Therefore the discharge behaviour of a metal halide GIC as cathodes was investigated[1,2]. The present study deals with the cyclisation behaviour of $CuCl_2$-graphite

EXPERIMENTAL

The $CuCl_2$-GICs were prepared with natural flake graphite (Kropfmühl, Bavaria, particle size 200-400μm). The graphite was heated with anhydrous copper chloride in a chlorine atmosphere[3] to give a first stage compound with a typical composition $C_5CuCl_{2.1}$. The structure was determined by X-ray diffraction. The composition was ascertained by means of pyrohydrolysis followed by chemical analysis.

Two different types of electrodes were prepared. Either the flakes were inclosed in a small platinum container[4], or the GIC was mixed up with a solution of two weight-percent ethylene propylene diene terpolymer in cyclohexane until a uniform pulp was formed, and coated on a flat platinum electrode[5]. At last the electrode was pressed with 50 kp/cm^2.

As the electrolyte, a 1 M solution of lithium perchlorate in propylene carbonate (PC) was used. The solution was dried in a column filled with 0.4 and 0.5 nm molecular sieve. All chemicals used were of reagent grade (Merck, Darmstadt). An Ag/AgCl electrode served as the reference electrode, the counter electrode consisted of platinum.

Three different electrochemical methods were applied: cyclic voltammetry, pulsed galvanostatic technique and AC impedance measurements. Cyclovoltammetric scans were performed by using a potentiostatic controller (model POS 73, Bank Elektronik, Göttingen). For the pulsed galvanostatic measurements this apparatus was combined with a double pulse control generator (model DPC 72, Bank Elektronik, Göttingen). Current pulses of 80 s were imposed on the working electrode. Subsequently, the circuit was interrupted for 220 s. Impedance measurements were carried out by means of a frequency response analyzer (NF-Electronic Instruments, Japan).

RESULTS AND DISCUSSION

In the cyclovoltammogram of the polymer electrode (fig. 1) a wide peak with a shoulder occurs at about 500 mV during the first cycle. This peak belongs to the reduction of Cu(II) to Cu(I), accompanied by deintercalation. The solution takes a yellow-brown colour. Beginning at -300 mV copper deposition can be observed.

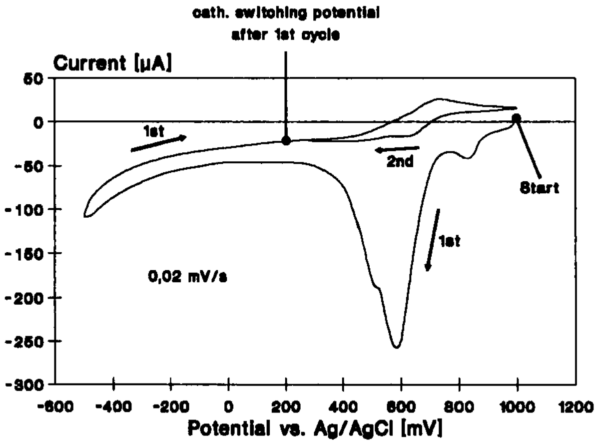

FIGURE 1 Cyclovoltammogram of $CuCl_2$ GIC in 1M $LiClO_4$/PC (polymer electrode), $m_{graphite}$: 145 mg.

An anodic wave being due to the reversible redox couple Cu(II)/Cu(I) appears at 650 mV. This corresponds to the situation of a platinum electrode in a $CuCl_2$/PC-solution (fig. 2). No further deintercalation at 500 mV occurs during the following cycles, neither after changing the electrolyte solution.

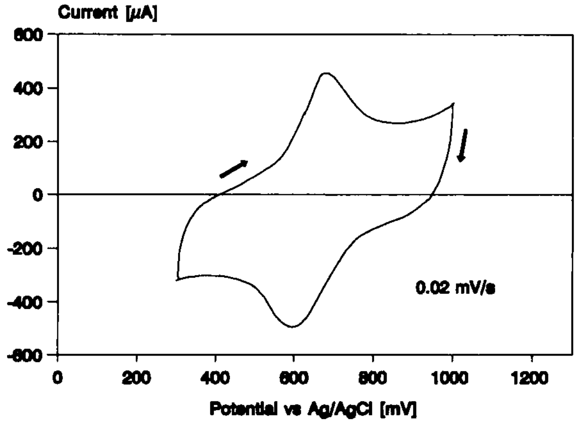

FIGURE 2 Cyclovoltammogram of platinum in 1M $LiClO_4$/PC saturated with anhydrous $CuCl_2$.

X-ray investigations prove that the first stage structure is retained after cyclisation. After saturating the electrolyte solution with anhydrous $CuCl_2$ the same cyclovoltammogram is observed. Therefore the deintercalation tendency does not depend on the copper concentration in the electrolyte solution. Using the platinum container electrode causes a better resolved CV curve. The cyclovoltammogram of the GIC in the platinum container electrode (fig. 3) shows that deintercalation and reduction occur in several steps. May-be the first peak which can also be seen in the cyclovoltammogram of the polymer electrode belongs to a side reaction, and the other sharp peaks depend on non equivalent spots.

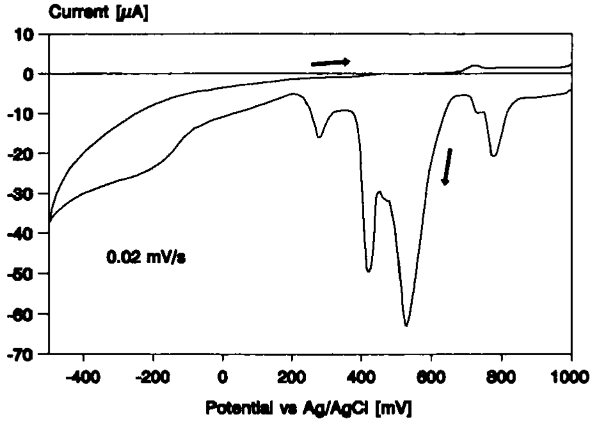

FIGURE 3 Cyclovoltammogram of $CuCl_2$ GIC in 1M $LiClO_4$/PC (platinum container electrode), $m_{graphite}$: 26 mg.

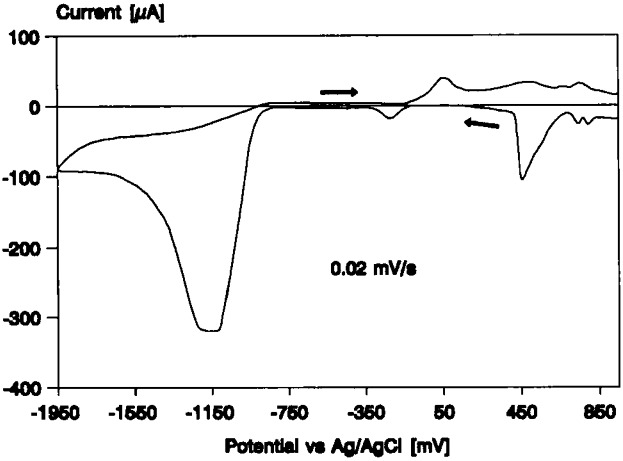

FIGURE 4 Cyclovoltammogram of $CuCl_2$ GIC in 1M $LiClO_4$/PC (platinum container electrode), $m_{graphite}$: 22 mg.

At lower potentials there is a much bigger peak. Below -1100 mV, intercalated Cu(II) species are reduced to metallic copper in a two-electron-transfer-step followed by deintercalation (fig. 4). This peak can also be seen in the cyclovoltammograms given by Yazami et al.[2]. The reaction is not reversible, only a very low anodic current can be detected upon the reverse scan. After the copper deposition the original layer structure was found to be completely destroyed.

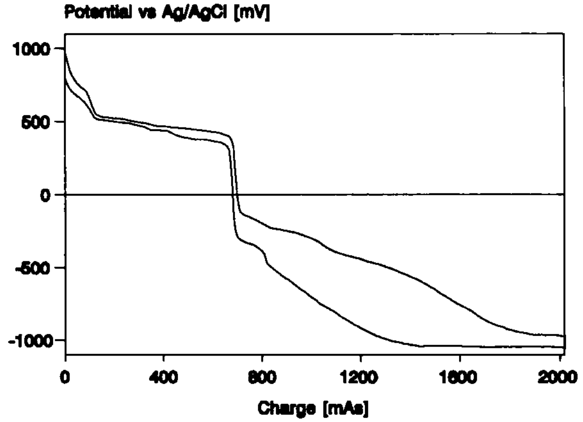

FIGURE 5 Pulsed galvanostatic reduction of $CuCl_2$ GIC in 1M $LiClO_4$/PC, $m_{graphite}$: 20 mg.

The potential curve obtained for pulsed galvanostatic reduction of $CuCl_2$ GIC shows three distinct plateaus (fig. 5). The first plateau belongs to the reduction of Cu(II) to Cu(I), accompanied by deintercalation, and corresponds to the wide peak at about 500 mV in the cyclovoltammogram. The second plateau corresponds to the reduction of Cu(I) which was formed in the first step. It is followed by a considerably long plateau for the reduction of Cu(II) to Cu, indicating that only small amounts of copper species participate in the other reactions.

The overpotential during the pulsed galvanostatic reduction can be seperated by means of AC impedance measurements. Therefore the DC was superimposed with an AC within a frequency range of 20 kHz to 1 Hz. The data of the total impedance were corrected for the inductance, the electrolyte resistance and the double layer capacitance to obtain the pure Faraday impedance[6]. The Nyquist-plots show that the charge transfer resistance is almost constant during the whole reduction process. The different overpotentials are due to different diffusion resistances. The lowest diffusion resistance was found at the first plateau corresponding to the reduction of Cu(II) to Cu(I) accompanied by deintercalation (fig. 6). Probably the copper species close to the surface of the GIC react upon this step.

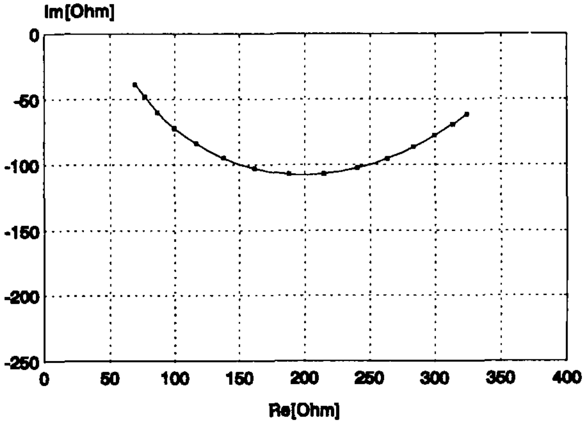

FIGURE 6 Nyquist-plot of corrected data (first plateau).

With ongoing the diffusion resistance is raised and reaches its maximum at the end of the second plateau (fig. 7). Probably the very high overpotential in this region depends partly on crystallisation resistance at the beginning of the copper deposition. This resistance is indicated in the corrected Nyquist-plot. The diffusion resistance decreases at the third plateau, corresponding to the reduction of Cu(II) to metallic copper.

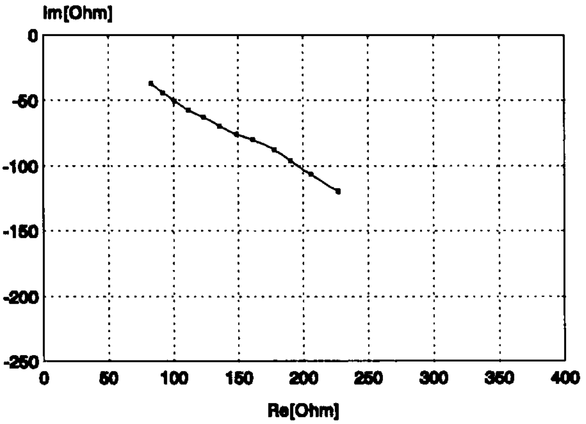

FIGURE 7 Nyquist-plot of corrected data (second plateau).

All the measurements show that the reduction of $CuCl_2$-graphite takes place in two different potential regions. A small amount of Cu(II) is reduced to Cu(I) and deintercalated at about 500 mV and further reduced to metallic copper around -300 mV. Most of the $CuCl_2$ is reduced to copper and deintercalated in a two-electron-transfer-step below -1100 mV. The deintercalation is irreversible.

REFERENCES

1. M. Armand, P. Touzain, Mater. Sci. Eng., 31, 319 (1977)
2. R. Yazami, P. Touzain, L. Bonnetain, Synth. Met., 7, 169 (1983)
3. E. Stumpp, Mater. Sci. Eng., 31, 53 (1977)
4. P. Scharff, habilitation thesis, Clausthal (1991)
5. R. Opitz, diploma thesis, Clausthal (1992)
6. P. Schmittinger, D.W. Wabner, Metalloberfläche Angew. Elektrochemie, 26, 262 (1972)