

THE ELECTRICAL CONDUCTIVITY OF POTASSIUM FERROCYANIDE UNDER PRESSURE

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Introduction

In the case of compressing directly the powder of alkali halide, such as AgBr, by means of piston without the pressure transmitting fluid, the relations between the electrical conductivity and pressure have been measured to 3,000 kg/cm² at room temperature¹⁻³).

In this experiment the variation of electrical conductivity under pressure for potassium ferrocyanide, used as an example of complex and hydrous crystals, is measured at room temperature up to a pressure of 14,100 kg/cm², higher than that used in the measurements of alkali halide.

Recently, the measurement of electrical conductivity under such ultra high pressure as 100,000 kg/cm² pressure at room temperature or below 200°C has been carried out only by P.W. Bridgman⁴⁻⁶) who used the powder of several semiconductors as a sample and pointed out the difficulty in the experiment.

Experimentals

(1) Samples

As it is well known⁷⁾ that the solid dielectrics have structure sensitive property (which is predominated by heat treatment, humidity and impurity, etc.) for the measurement of electrical conductivity at room temperature and atmospheric pressure, the purity of the sample used must be taken into consideration. Therefore, the sample is purified by the following three methods of recrystallization from potassium ferrocyanide made by Merk.

A small quantity of impurities in the sample is detected by qualitative analysis⁸⁾: only three ions, CO₃^{''}, SO₄^{''} and Cl['].

Sample a: Potassium ferrocyanide from Merk is used. A very small quantity of CO₃^{''} and SO₄^{''} is present.

- 1) I. Shapiro and I. M. Kolthoff, *J. Chem. Phys.*, **15**, 41 (1947)
- 2) I. Shapiro and I. M. Kolthoff, *J. Phys. Colloid Chem.*, **52**, 1319 (1948)
- 3) W. Jost and G. Nehlep, *Z. Phys. Chem. (B)*, **34**, 348 (1936)
- 4) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **79**, 125 (1951)
- 5) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **79**, 149 (1951)
- 6) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **81**, 165 (1952)
- 7) E. Koch and C. Wagner, *Z. Phys. Chem. (B)*, **38**, 295 (1937)
- 8) L. Vanino, *Handbuch der Preparative Chemie* (1), 398 (1925)

Sample b: Recrystallized from an aqueous solution of the sample a. A very small quantity of $\text{CO}_3^{''}$ is present.

Sample c: Crystallized in a desiccator with conc. H_2SO_4 at room temperature from the residue solution which is already separated from the sample b. Namely, the sample contains more impurities than the others. A small quantity of $\text{CO}_3^{''}$ and a very small quantity of $\text{SO}_4^{''}$ are present.

Sample d*: Potassium ferrocyanide is dissolved in a 1% KCN solution and the solution obtained is allowed to remain for a day. Alcohol is then added and potassium ferrocyanide is obtained as a white crystalline precipitate. A very small quantity of $\text{CO}_3^{''}$ and Cl' is present.

Sample e*: Potassium ferrocyanide is dissolved in a 1% dilute acetic acid and the solution obtained is allowed to remain for a day, being separated completely from air. Then, the solution is filtered and mixed with alcohol, and purified potassium ferrocyanide is obtained as a cream coloured crystalline precipitate. A very small quantity of Cl' is present and $\text{CO}_3^{''}$ not present.

Sample f (Anhydride): It is prepared by heating the sample b at 110°C in an air thermostat for an hour.

Before every experiment the sample of 250 mesh fine powder is kept in a desiccator with the relative humidity 71% for 24 hours, except in the case of the sample f, in order to avoid the effect of humidities in the air.

(2) Method of measuring electric resistance

When a static field is applied to potassium ferrocyanide or its anhydride at a given pressure, it is known by colouring with the indicators that the electrolytic conduction occurs, but, in the case of the application of alternating field the electrolysis is not observed.

Therefore, it is measured by the Kohlraush bridge which is assembled with the Hartley circuit oscillator and a low frequency two stage amplifying detector.

(3) High pressure apparatus and electrodes

The high pressure apparatus used for the present experiment has been already reported¹²⁾.

The electrodes are set between the upper and the lower pistons of the intensifier, and then the compression is two dimension. This is shown in Fig. 1.

The materials of the electrodes are 13 Cr-steel or tungsten carbide. The tungsten carbide electrodes are constricted exteriorly with a steel ring in order to increase their

* Briggs reported in his first study⁹⁾ that the isomers were prepared by the methods of recrystallization used on samples d and e, but afterwards¹⁰⁾ he pointed out them as identical. On the other hand, Getman¹¹⁾ denied the existence of the isomers by means of absorption spectra.

9) S. H. C. Briggs, *J. Chem. Soc.*, 99, 1019 (1911)

10) S. H. C. Briggs, *J. Chem. Soc.*, 117, 1026 (1920)

11) F. H. Getman, *J. Phys. Chem.*, 32, 187 (1928)

12) R. Kiyama and T. Yanagimoto, *This Journal*, 21, 32 (1951)

strength and prevent from danger. The surface of the electrode is 8mm in diameter. In the case of above $7,000 \text{ kg/cm}^2$ the electrode of tungsten carbide is used* instead of 13Cr-steel because the surface of the 13Cr-steel electrode in both sides deforms to concave.

Between the pistons and the electrodes is used mica as an insulator**.

(4) Operations

About 30mg of the sample placed between the two electrodes is compressed gradually to a definite pressure and the resistance is measured by Kohlraush's bridge. During the course of the experiment the curved surface of the electrodes are covered with the "Electron Compound" for insulating in order to avoid the effect of moisture in the air as shown in Fig. 1.

The thickness of the sample is measured without delay by means of a micrometer after the pressure has been released and its value is about $0.14 \sim 0.15 \text{ mm}$. The difference of the thickness of the sample in the course of compression and that after being released is checked by the use of a cathetometer, and it is within 0.01 mm .

Making the sample about twice as thick, the specific resistance does not change.

Results

(1) When the powder of potassium ferrocyanide is gradually compressed up to $5,000 \text{ kg/cm}^2$ at room temperature, it becomes semitransparent and above $7,000 \text{ kg/cm}^2$ transparent as if it were melted. The prolonged duration of compression increases transparency, but, after the pressure has been released, as the sample is allowed to remain in the air at room temperature, the gradual decrease of transparency is observed with naked eye.

In the case of anhydride, even though compressed to the same degree it does not become semitransparent, and forms only a powder cake.

(2) At a definite pressure the specific resistance ρ of samples decreases with the time and reaches to a constant value after about 2 hours, but, in the case of sample e it reaches to a constant value increasing with time as exemplified in Fig. 2.

* Though it is known⁹ that the material of tungsten carbide is deformed by the pressure of several ten thousand kg/cm^2 , under this experimental condition it is not.

** It is confirmed experimentally that the specific resistance of mica is enough larger under the pressure range from 1 to $20,000 \text{ kg/cm}^2$, and therefore mica is able to be used as an insulator.

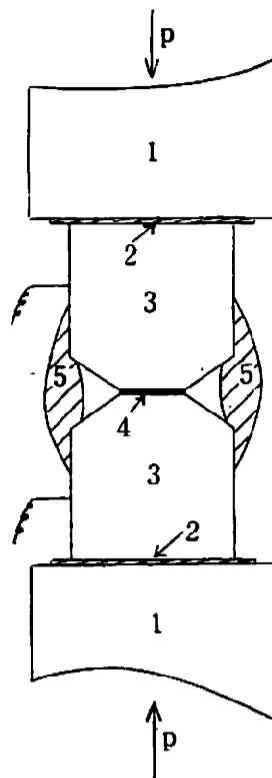


Fig. 1

- 1 : Piston
- 2 : Mica
- 3 : Electrode
- 4 : Sample
- 5 : Electron compound

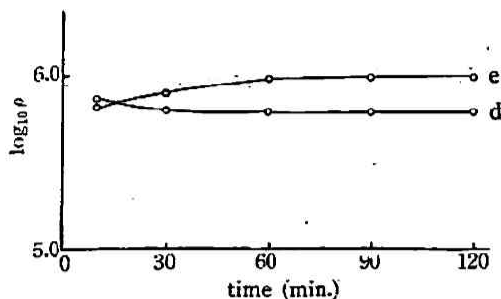


Fig. 2
7,000 kg/cm², 20°C

are decreased by the compression, the conductivity decreases in obedience to Smekal's consideration¹³⁾ for the surface conductance.

Therefore, it is considered naturally that the minimum points of the specific resistance against pressure curves are found by the above contrary expectation. In this experiment, at 1,410 kg/cm² the minimum points are found as shown in Fig. 3. These results are analogous to Kolthoff's experiments^{1,2)} on AgBr.

And moreover, it may be considered that above 1,410 kg/cm² the increase of specific resistance is due to not only the decrease of surface but also the decrease of the mobility of ions and the number of defect frozed in at a definite temperature^{14,15)}.

(4) It is known⁷⁾ that a small quantity of impurity increases the electrical conductivity extraordinarily. In this experiment the specific resistances of recrystallized samples have about 10⁶ ohm·cm in the pressure range from 200 to 14,100 kg/cm² in spite of the use of the different recrystallization process, and it is known that the recrystallized samples are much purer than the starting sample.

On the other hand, according to the comparison with the specific resistances of the samples a, b and c which contain different quantity of impurity at a definite pressure the influence of impurity shows that the specific resistance value of sample b is 10 fold to a and 100 fold to c as shown in Fig. 3. That is to say, the smaller the sample contains impurity the larger specific resistance.

(3) The variation of such constant specific resistance with pressure is shown in Fig. 3.

Compressing the powder, may occur the following two expectations simultaneously.

i) As the powder is compacted the contact between the grains increases and the conductivity increases.

ii) As the internal and external surfaces

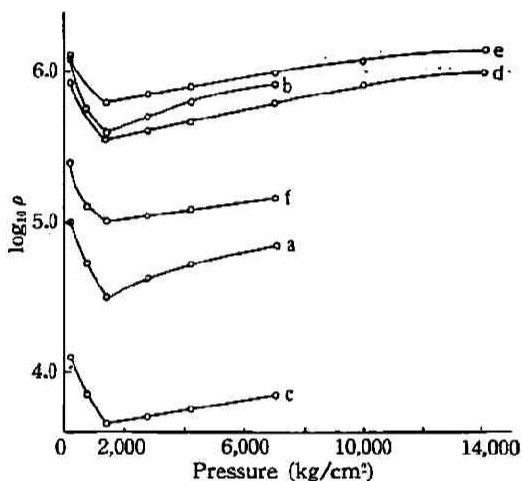


Fig. 3
Sample a, b, c and f at 25°C
Sample d and e at 20°C

13) A. Smekal, *Handbuch der Physik* 24 (part 2) 881 (1933)

14) W. Jost, *Trans. Farad. Soc.*, 34, 860 (1938)

15) N. F. Mott and R. W. Gurney, *Electronic Process in Ionic Crystal*, p. 40 (1940), Oxford.

(5) At room temperature and atmospheric pressure, it is known¹⁶⁾ that the hydrous crystal is a good insulator and the water of crystallization does not act for the electrical conductivity. Though the relation of conductivity of hydrous crystal and anhydrous one under pressure has been studied until now, this experimental result indicates that the part of water of crystallization is not particularly observed up to 14,100 kg/cm² comparing the hydrous with the anhydrous for the form and minimum point of specific resistance against pressure curve.

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16) H. Saegusa and T. Matsumoto, *Sci. Rept. Tohoku Univ.*, 28, 235 (1939)