

CONDUCTIVITY MEASUREMENTS ON PURE AND MIXED METAL DIOXIDES*

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Summary

A new low pressure method of power conductivity measurement is presented. Results are relatively reproducible. No significant differences have been found resulting from grain size. Activation energies have been calculated for β MnO_2 : 0.10 eV and for γ MnO_2 : 0.48 eV. Molar water content and electrochemical activity depend on the method of preparation. Ozone precipitated γ MnO_2 shows an apparent relationship between conductance and acidity of the solution used in its preparation. Ozone precipitated PbO_2 is electrochemically inactive but has a high conductivity. Mixed Mn/Pb metal dioxides show different structures. There is a minimum in conductance at the 1:1 molar mixture. A schematic model is given for the mechanism of semiconductivity in solids containing OH groups and having a $[\text{MeO}_6]_x$ type structure.

Résumé

Une nouvelle méthode de mesure de la conductivité à basse pression pour solides pulvérulent est introduite. Les résultats sont relativement reproductible, il n'y a des différences significatives entre la grandeur des particules du poudre. L'énergie d'activation est obtenue pour β MnO_2 : 0.10 eV et pour γ MnO_2 : 0.48 eV. L'eau molaire et la résistivité dépendent des méthodes de la préparation. γ MnO_2 précipité par l'ozone montre une relation évidente entre la conductivité et l'acidification préalable de la solution primaire. PbO_2 précipité par l'ozone ne donne aucune activité électrochimique, mais possède une bonne conductivité. Les oxides mixtes du Pb et Mn apparaissent avec différentes structures. Il existe une résistivité minimale pour une combinaison

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molaire 1:1. Finalement, on présente un modèle schématique sur le mécanisme de la semiconductivité en corps solides avec les groupes OH et la structure $[\text{MeO}_6]_x$.

Zusammenfassung

Es wird eine neue Methode zur Messung der Leitfähigkeit fester Pulver vorgestellt. Die Pulver werden dabei keinem besonderen Vordruck unterworfen. Die Messergebnisse bleiben relativ und sind reproduzierbar. Die Korngrösse hat innerhalb des Arbeitsbereiches keinen wesentlichen Einfluss. Die Aktivierungsenergie für β MnO_2 liegt bei 0.10 eV und für γ MnO_2 bei 0.48 eV. Der molare Wassergehalt und die elektrochemische Aktivität hängen von der Herstellungsmethode ab. Ozongefälltes γ MnO_2 zeigt eine deutliche Abhängigkeit des Leitwertes von der Aktivität der Fällungslösung. Ozongefälltes PbO_2 ist elektrochemisch inaktiv, hat aber eine hohe elektrische Leitfähigkeit. Mn/Pb Mischmetall-Dioxide zeigen verschiedene Strukturen. Das Minimum des Leitwertes liegt bei Molverhältnis Mn/Pb wie 1:1. Es wird ein Modell für den Mechanismus der Halbleitung für OH-haltige Festkörper mit einer Basisstruktur von $[\text{MeO}_6]_x$ gegeben.

Introduction

From the literature it can be seen that almost every method has been used to measure the conductivity of semiconducting powders. Some experiments have been carried out using a.c., others using d.c. Solid specimens have been investigated as well as powders compressed at high pressures.

McBreen [1], in 1975, gave a diagram, shown in Fig. 1, for the variation of conductivity with pressure of a number of manganese/oxygen compounds. From this Figure it is apparent that the electrochemically active gamma variety of MnO_2 has a much lower conductivity than the inactive beta- MnO_2

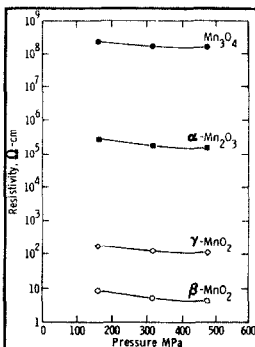


Fig. 1. Resistivity of MnO_{1+x} phases according to McBreen [1].

phase. Contrary to the method of Glicksman and Morehouse [2], which was also used by McBreen, we have tried to measure the conductivity of these two kinds of MnO_2 in a totally different way. At first we tried to minimize the ohmic contribution of the components of the apparatus, but this was not successful as the results obtained were not sufficiently reproducible. Finally, we found that satisfactory results could be obtained if we measured the conductivity with the minimum application of pressure. The method requires, however, that the same standardised procedure and method of handling be used for every sample to be examined.

Experimental

Our first samples were well ground in a laboratory mill for about one hour. Before we recognized that grain size had no influence on the measurement, we sieved every sample into three fractions. Later, we only ground for 10 min, by hand, in a porcelain mortar. The powdered samples were then placed in the measuring apparatus which consisted of a simple graduated glass cylinder with two internal brass pistons. The faces of the pistons in contact with the powdered material were gold plated. The powder-filled tube with the lower piston in position was then shaken 1 000 times in a vibration machine, after which the upper piston was placed in position with a weight of 2 kg on top to ensure good contact between it and the mass of the powder; the area of the piston was 1.767 cm^2 and the pressure applied 1.13 kg/cm^2 (111 kPa). Figure 2 shows the arrangement schematically.

The actual electrical measurements were made with a Wheatstone bridge using d.c. Figure 3 shows the two parts of the apparatus. The lower base plate is made from Teflon; the cement material for holding the glass tube must be temperature resistant.

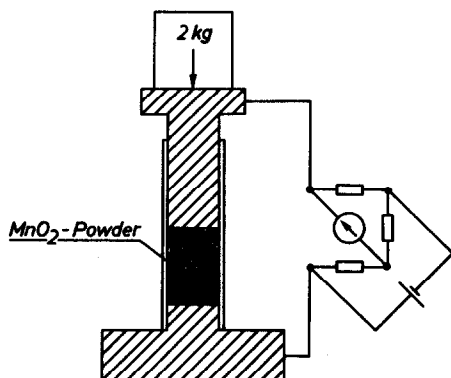


Fig. 2. Method of measuring resistance of MnO_2 powder.

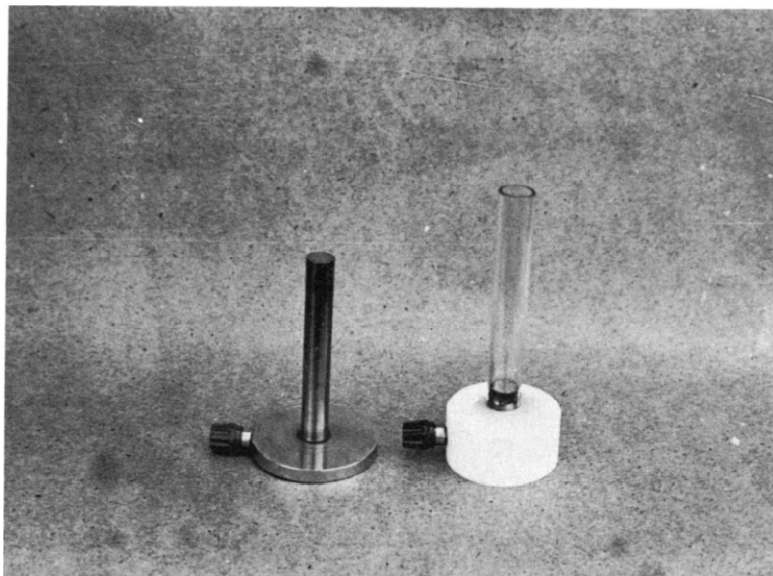


Fig. 3. Elements of the apparatus for resistance measurements.

Results

With this method we obtained values of resistance which are generally higher than those of other workers, but the temperature dependence was reproducible. Figure 4 shows the first results obtained with different grain sizes sieved from the same MnO_2 sample.

It is apparent that the resistivity decreases with temperature, but grain size has little effect and so its influence can be neglected. Consequently, we no longer sieve the ground samples, but we still grind them for a more closely controlled period of time. Figure 5 shows the variation of conductivity with temperature for samples of β MnO_2 and γ MnO_2 (IC sample number 1). For both materials there is a linear relationship between the logarithm of the conductivity and $1/T$.

Using the formula for semiconductor conductivity

$$\sigma = A \cdot e^{-B/T},$$

we derived the activation energies, given in the last line of Table 1, between 273 and 353 K for the two varieties of MnO_2 . Comparing our results with the values published by other workers using different methods, we find that there is agreement in both cases. In Fig. 6 we have gathered together all our conductivity data for the various types of γ MnO_2 . On this diagram areas have been marked enclosing the values for materials obtained by different chemical or electrochemical methods of preparation. Our ozone-prepared γ MnO_2 has the worst electrical quality (conductance), but a very high elec-

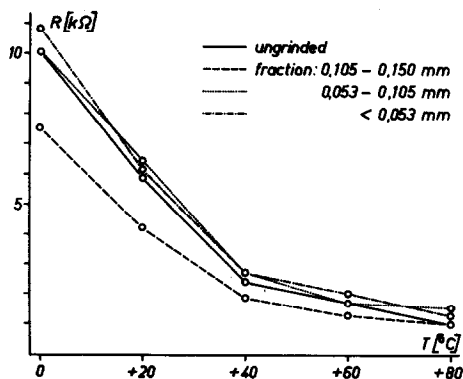
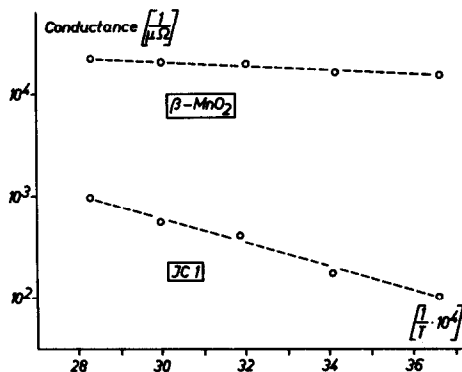
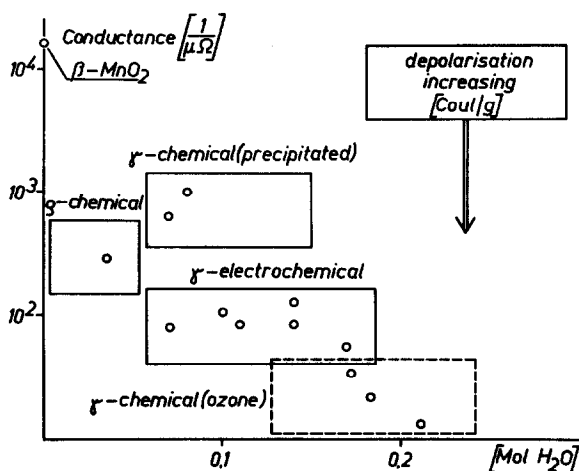
Fig. 4. Variation of MnO_2 resistivity vs. temperature.Fig. 5. Variation of MnO_2 conductivity vs. $1/T$.

TABLE 1

Activation energy of β and γ MnO_2

Authors	Year	β MnO_2 (eV)	γ MnO_2 (eV)	Literature
Wiley and Knight	1964	0.05	—	[3]
Bhide and Damle	1960	0.30	—	[4]
Brenet and Declerk	1956	—	0.51	[5]
Chevillot and Brenet	1960	0.26	0.70	[6]
Brenet and Faber	1977	0.10	0.48	[this work]

Fig. 6. Relation between the electrochemical reactivity of MnO_2 and its water content.

trochemical activity in Coulomb/gram. Furthermore, the best conductance value is shown by β MnO_2 , which has no water content (upper left). The water content is estimated according to the formula of Brenet [7].

From the data of Fig. 6 we are able to recognize the following clear relations:

(1) The better the conductivity, the worse the electrochemical reactivity.

(2) The better the conductivity, the lower the analysed water content.

This is also in agreement with the work of Ruetschi [8], who showed that there is a logarithmic dependence of conductivity on the total water content. This diagram is reproduced here in Fig. 7.

If our two premises are correct, then a further correlation can be drawn from Fig. 6: the more water that is bound within the molecular geometry of the active MnO_2 structure, the greater is the electrochemical activity. This correlation is, in fact, found with all the γ MnO_2 which we prepared by precipitation with ozone from acid solutions of manganese(II) salts. The precipitation of MnO_2 species by oxidation with ozone is a very simple means of obtaining highly electrochemically active material. A manganese(II) salt, preferably the perchlorate, is dissolved in water and gaseous ozone from a laboratory ozone generator is bubbled through the solution. The more acidic the starting solution, the lower is found to be the conductivity of the ozone-produced MnO_2 sample, *i.e.*, the more protons that are initially present, the lower is the conductivity and the higher the electrochemical activity. Figure 8 shows this trend diagrammatically.

Encouraged by the simple procedure of preparing active MnO_2 by reaction of ozone with aqueous solutions, we then attempted to apply our experience to the preparation of PbO_2 , a material of great importance in its electrochemically-active form for secondary batteries.

We found that this too could be precipitated by the action of ozone on acetic acid solutions. In perchloric acid solutions Pb(II) ions could not be oxidised by ozone, which means that no PbO_2 is precipitated. The PbO_2 we

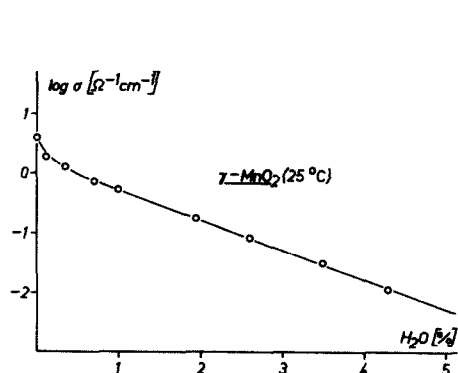


Fig. 7. Relation between the conductivity of MnO_2 and its water content according to Ruetschi [4].

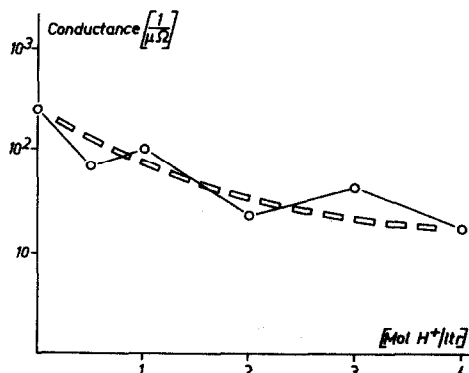


Fig. 8. Conductivity of MnO_2 as a function of the H^+ content in the acid solution.

obtained by the action of ozone on Pb(II)-acetate solutions was unfortunately quite inactive electrochemically. It was a good electronic conductor and contained almost no water. It was, in fact, very similar to the PbO₂ powder which can be bought commercially (Product Fa. Merck, Germany), although this commercial PbO₂ is not prepared using ozone. We measured the change of conductivity with temperature of these two pure forms of PbO₂. The results are shown in Fig. 9. Both materials show a linear relationship with a shallow slope. This behaviour is similar to that of β MnO₂. Because of the relation between β MnO₂ and our first PbO₂ preparations we considered it would be of interest to study mixed manganese/lead dioxides to determine whether these metal dioxides, crystallising in the same habit, showed any electrochemical activity in the mixed form. The preparative procedure is again very simple. We mixed manganese and lead acetate solutions and treated the mixture with ozone. The formula of the basic reaction is given in Fig. 10.

We examined different molar proportion (a:b) Mn:Pb mixtures that we had precipitated with ozone. The result of this experimental series was surprising. Figure 11 gives a schematic indication of the range of products obtained. In the area of 1:1 molar proportion Mn/Pb, X-ray structural analysis shows rutile-type dimensions. Other mixtures were found to be amorphous. If the molar relationship is changed to 10:1 (Mn/Pb) the structure also changes from the tetragonal to the orthorhombic form, which is similar to that of pure γ MnO₂. These results are summarised for greater clarity in Table 2, where structural data are given.

The X-ray diagrams for pure γ MnO₂, the MnO₂/PbO₂ mixture (1:1) and pure β PbO₂ are shown in Fig. 12. Also, scanning electron micrographs of the mixed MnO₂/PbO₂ (1:1) preparation are given in Figs. 13 and 14. Figure 13 shows samples, precipitated at room temperature (left) and at

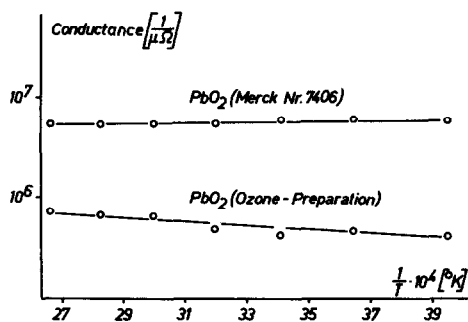


Fig. 9. Conductivity of PbO₂ vs. 1/T.

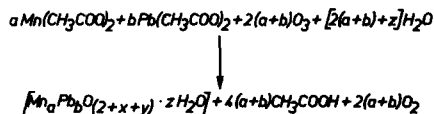


Fig. 10. Schematic formula for the preparation of MnO₂/PbO₂ mixed phases.

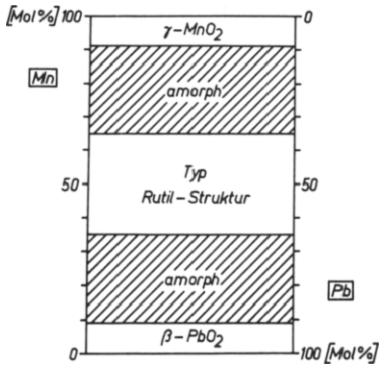


Fig. 11. Domains of crystalline structures for different contents of Pb and Mn in mixed Pb/Mn oxides.

TABLE 2

Crystalline parameters of different structures of Pb/Mn dioxides

β PbO ₂ (product Merck)		MnO ₂ /PbO ₂ (1:1)
$a = 4.93 \text{ \AA}$		$a = 4.92 \text{ \AA}$
$b = 3.37 \text{ \AA}$		$b = 3.36 \text{ \AA}$
	tetragonal	
	↑	
	orthorhombic	
	↓	
γ MnO ₂ [9]		MnO ₂ /PbO ₂ (10:1)
$a = 4.42 \text{ \AA}$		$a = 8.55 \text{ \AA}$
$b = 9.70 \text{ \AA}$		$b = 7.53 \text{ \AA}$
$c = 2.79 \text{ \AA}$		$c = 4.40 \text{ \AA}$

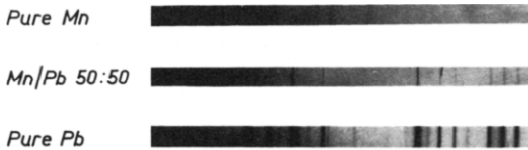
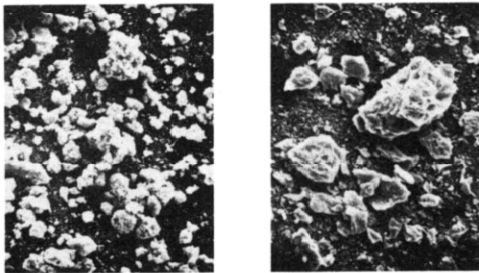


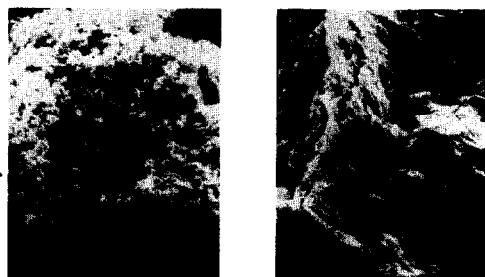
Fig. 12. X-ray diagrams of different Pb/Mn oxides.



1 : 400

+25 °C Mn/Pb +70 °C

Fig. 13. Scanning electron micrograph of Pb/Mn oxides.



1 : 4 000

+25 °C

Mn/Pb

+70 °C

Fig. 14. Scanning electron micrograph of Pb/Mn oxides.

70 °C (right), at a magnification of 400 times. Figure 14 shows the same material at a magnification of 4 000 times.

The conductance (conductivity) diagram for the mixed $\text{MnO}_2/\text{PbO}_2$ phases is given in Fig. 15. It will be seen that there is a wide range of conductivity values for the different molar proportions of $\text{MnO}_2/\text{PbO}_2$ mixtures prepared by simultaneous precipitation.

The lowest conductivity was found in the middle range where we found 1 micro-Siemens and the tetragonal structure of pure β PbO_2 still predominates. Pure β PbO_2 itself has a conductivity of *ca.* 1 Siemens, that is, one million times greater. The water content of the mixed dioxides is at a maximum in the middle range also. This latter fact coincides, in general, with our experience of the relationship between water content and conductivity value. All mixed dioxides prepared by the direct action of ozone on aqueous solutions were electrochemically inactive.

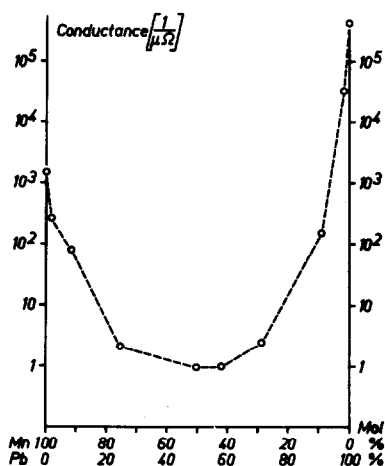


Fig. 15. Conductivity of Pb/Mn oxides as a function of Pb/Mn ratio.

Finally, we show in Fig. 16 the change of conductivity with temperature for the MnO_2/PbO_2 (3:1) mixed sample. As expected, the diagram is of linear form with a rather steep slope of conductance increasing with fall in temperature.

Using the previously mentioned formula for semiconductor conductivity, a calculation of the activation energy gives a value of 0.67 eV.

Conclusions

Arising from this work we are able to propose a schematic model for the conductivity mechanism in proton containing semiconductor structures. Our model uses $[MeO_6]_x$ structures as recommended by Burns and Burns [10] for the MnO_2 varieties. The model is a general one; it can be applied also to PbO_2 or other solid conducting species. For example, the model can be transformed to the case of solid electrolytes where, instead of protons, other cations are moving through a matrix of oxygen or nitrogen atoms:

- Sodium in β -AlOOH
- Lithium in TiS_2
- Lithium in Li_3N

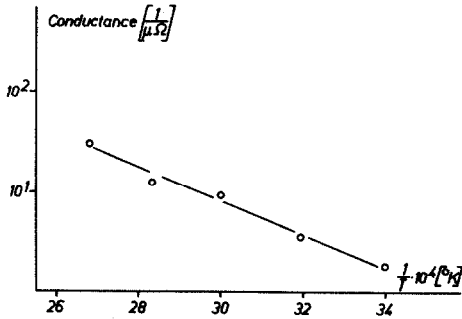


Fig. 16. MnO_2/PbO_2 conductivity vs. $1/T$.

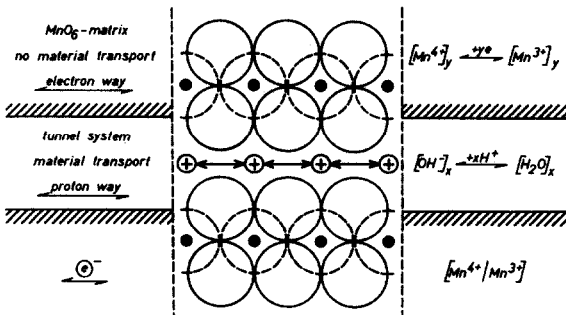


Fig. 17. Proton-electron conductivity model for γ MnO_2 phases.

In every case we have one positive partner moving and electrons transferring, or hopping, into the fixed molecular structure. Figure 17 shows the schematic model for the case of protons tunneling through a Burns type $[\text{MnO}_6]_x$ matrix.

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