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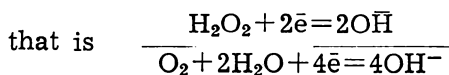
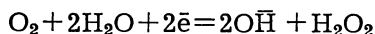
THE USEFULNESS OF THE TIP-POINT MICRO ELECTRODE
IN THE MEASUREMENT OF ODR IN SOIL

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Agrophysics of the Polish Academy of Sciences of Lublin

INTRODUCTION

The measurement of the oxygen diffusion rate (ODR) in soils was introduced by Lemon and Erickson [2] as an index of oxygen availability for plant roots. The principle of the method consists in diffusion current measurement during the polarographic reduction of oxygen on the platinum electrode which simulates the plant root. This method has been applied, up to now, in a lot of tests. The results of these experiments, however, in many cases, gave diverging results, which was caused by methodical difficulties connected with the influence of soil resistance on the measurement and the lack of a distinct polarographic plateau corresponding to oxygen reduction in unsaturated soils. The first difficulty connected with the elimination of the influence on the measurement has already been solved [1] but an understanding of the lack of the polarographic plateau requires definition. It is known that the plateau exists in water suspensions and in soils saturated with water. McIntyre in his excellent review of ODR method [4] suggests that the decay of the plateau in unsaturated soils may be caused to two processes. One is the accumulation of OH⁻ ions on the electrode surface, which may cause a decay of current control by oxygen diffusion flux to the electrode. Another reason may be activation polarisation, connected with an insufficient reaction rate on the electrode surface.

The reduction process on the electrode surface according to McIntyre [4] is as follows in the pH range 4-12:



Hydroxyl ions are removed from the surface of the cathode under the action of two kinds of driving forces. The first of them is the concentration gradient causing diffusion from the cathode to the soil and the second one is the electric field applied causing a flow of anions from the cathode to the anode.

In the case of water solutions, suspensions, and soil fully saturated with water the possibility of carrying off hydroxyl ions from the cathode surface is high, because the migration takes place in the liquid phase engaging a considerable space, at least 40% of the total soil volume of the saturated soil.

In unsaturated soil, water in voids is partly replaced by air which is unavailable for OH^- ions migration. On the other hand the amount of oxygen reduced on the cathode increases due to the higher diffusion rate in air filled spaces and thus the amount of OH^- ions produced increases. The decreased migration possibility causes an accumulation of OH^- ions on the cathode surface and this slows the speed of reduction, as well as possibly causing a lessening efficiency in the second reaction i.e. the reduction of H_2O_2 . The application in that situation of a greater negative voltage to the cathode should increase the speed of migration of OH^- ions in the electric field as well as increase the speed of the cathode reactions and in effect cause a rise in the current intensity.

The outcome of this, is that if control of the current by diffusion declines as a result of OH^- ions accumulation on the cathode due to too narrow water paths enabling ion migration, then the lessening of the production of hydroxyl ions by decreasing the electrode surface should offer the opportunity of obtaining a plateau at least in the lower suction range.

The aim of the present work was to verify experimentally this hypothesis by a comparison of the conventional platinum cathode 0.5×4 mm and two multiple tip-point microelectrodes made of platinum wires of diameter 0.1 and the 0.04 mm. The surface of singular contact of Pt with the soil for the two latter electrodes was 825 and 10 600 times smaller, respectively.

MATERIALS AND EXAMINATION METHODS

ELECTRODES

The electrodes are built as shown in Fig. 1. The tip-point electrodes have been constructed in a multiple from in order to obtain measurable currents. Distances between the contact points with the soil were greater than 5 mm, to avoid a mutual interaction of the OH^- ion transport on their surfaces.

APPARATUS

Measurements were made by the use of the ODR measuring apparatus [3] enabling automatic control of effective reduction voltage.

FIELD TRIALS

The field measurements were carried out on the gray-brown podsollic soil in the vicinity of Lublin. On the experimental plot (2×2 m) after digging two tensiometers were installed. Then the soil was irrigated with a 40 mm water dose and current-voltage relations were measured at suction values 0 (water on the soil surface), 80, 150, 200 and 250 mb. Between measurements the soil was covered by plastic foil in order to

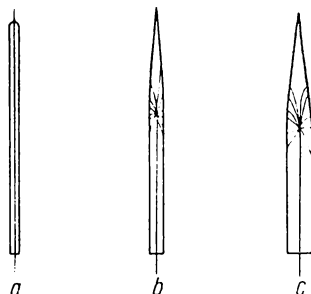


Fig. 1. Diagram of the electrode construction

a — conventional electrode 0,5×4 mm, *b* — tip-point microelectrode of 0,1 mm Pt wire, *c* — multiple tip-point microelectrode of 0,04 mm Pt wire. Size factor 1:1

provide possibly uniform moisture distribution in the surface layer. The electrodes were placed at a depth of 10 cm, current-voltage relations were taken by polarizing the platinum cathodes with voltages from 0 to 1.1 V with respect to the saturated calomel electrode (SCE) in divisions of 0.1 V. At each value of the polarisation voltage readings were taken after 3 min of polarisation, and then the voltage was raised by 0.1 V and so on. The soil temperature was from 2 to 5°C.

LABORATORY EXAMINATIONS

Chernozem soil from Werbkowice (0–30 cm) was employed for the laboratory work. Laboratory studies comprised comparative measurements of the diffusion current on oxygen concentration in the soil air as well as current-voltage relations comparison for all the three types of electrodes studied at different soil suctions and at different oxygen contents.

Studies of the influence of oxygen content on the diffusion current. The studies were performed in a funnel 10 cm high and 10 cm in diameter with a sintered glass plate with air-

-entry value 250 mb shown in Fig. 2. The soil sifted through a 3 mm sieve was placed in the funnell and after establishing a desired suction value (10,60 and 110 mb), gas mixtures containing from 0 to 21% of oxygen were introduced. Current intensity was read after obtaining the same oxygen concentration at gas inlet and outlet, using a polarization voltage of 0,65 V with respect to SCE and polarization time 3 min. The electrodes were introduced into the soil through holes in the plastic cover and sealed air tight. Oxygen concentration was measured with a Fieldlab oxygen analyzer (Beckman). The gas mixtures were obtained by using a needle valve adjusting the flow of nitrogen to the air. Firstly measure-

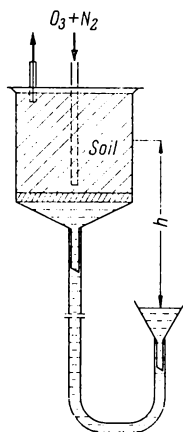


Fig. 2. Diagram of the suction plate used in the laboratory to establish soil suction

ments were made in pure air and afterwards in the gas mixture with a successively decreasing oxygen contents. After all the readings were taken, the electrodes were removed and cleaned by abbrasion with a tissue and rinsing in disilled water. The water level in the funnel was then lowered, and after four dalys the next set of measurements was taken.

Studies of current-voltage relations at different soil suctions and oxygen concentrations. The studies were performed in the same funnel shown in Fig. 2. The electrodes were inserted into the soil of a predetermined suction value (measured with respect to the middle of the soil layer and then current-voltage relations were taken in $-0,2$ to $-0,8$ V interval in $0,1$ V divisions and 3 min polarization time. During one set of measurements, the oxygen content in the soil was kept constant, and then the next set of measurements was performed at another oxygen concentration.

RESULTS AND DISCUSSION

The results of field studies are shown in Fig. 3. There is a distict polarographic plateau of oxygen reduction which holds from $-0,4$ to

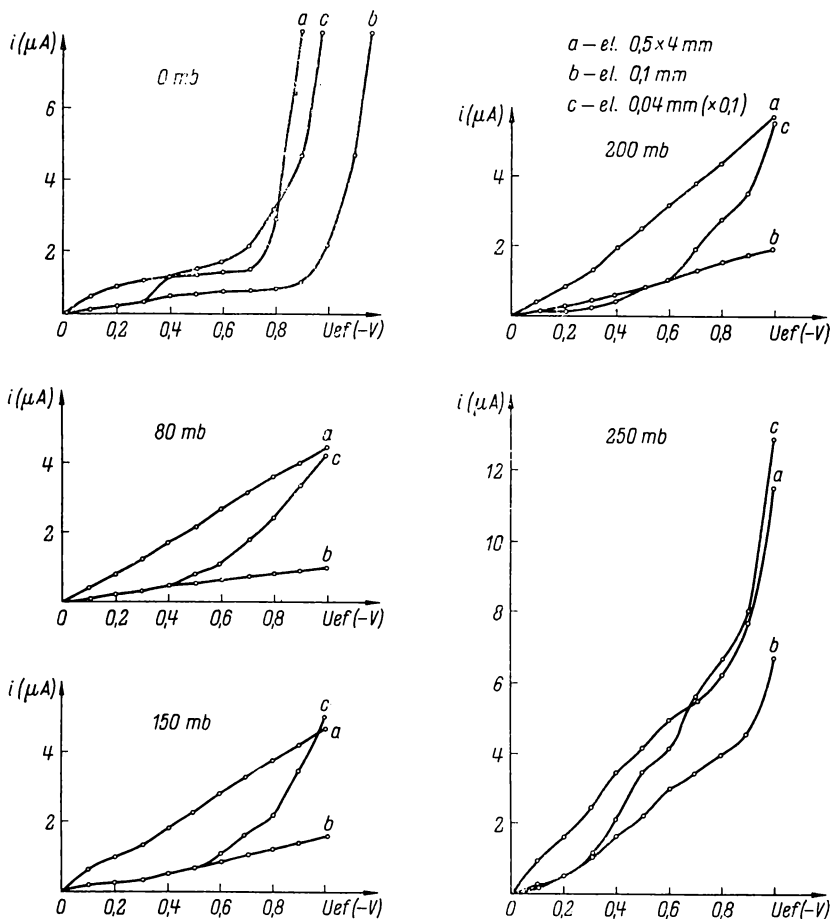


Fig. 3. Current-voltage relations of the three electrode types used obtained from field studies (current intensity for the c electrode is multiplied by 10)

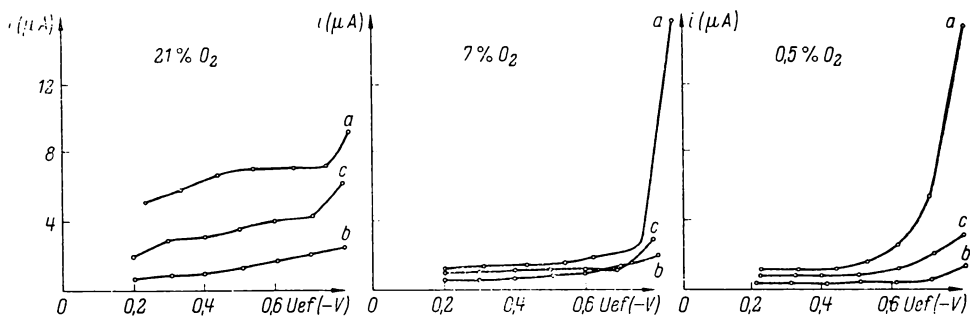


Fig. 4. Current-voltage relations obtained in the laboratory at 5 mb suction (current for the c electrode is multiplied by 10) denotations — as in Fig. 3

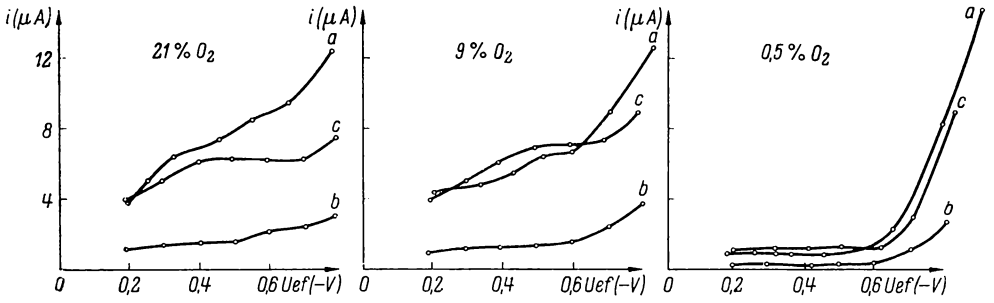


Fig. 5. Current-voltage relations as 25 mb suction (current for the c electrode is multiplied by 10)
denotations — as in Fig. 3

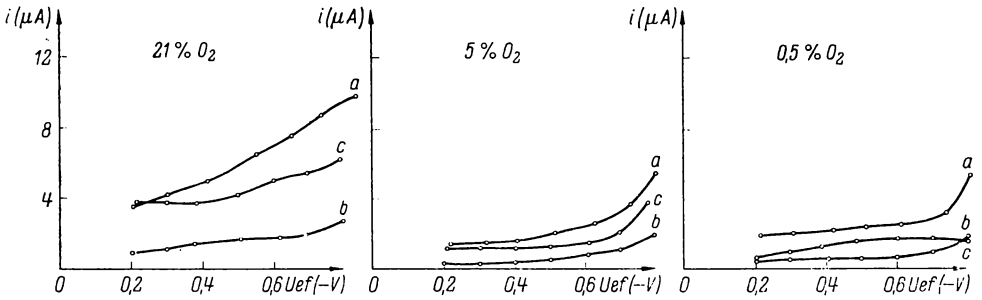


Fig. 6. Current-voltage relations at 40 mb suction (current for the c electrode is multiplied by 10)
denotations — as in Fig. 3

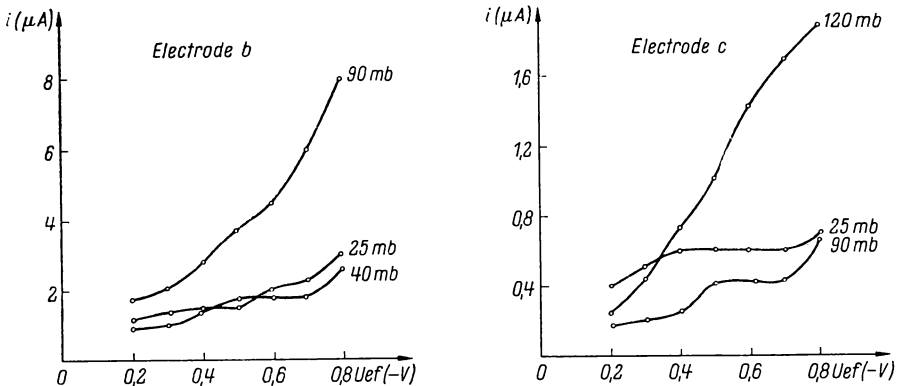


Fig. 7. Current-voltage relations for a and c electrodes at different suction values

$-0,7$ V for all the types of electrodes studied in a water saturation of the soil. For other suctions, however, none of the electrodes shows any trace of a plateau. The electrode *c* is distinguished by the strongest relationship of the current on the voltage which is parabola shaped, while the electrodes *a* and *b* have linear characteristics. Thus for 80–250 mb suction range, no plateau was found, and the laboratory studies a lower suction range was included.

The current-voltage relations obtained for suctions 5, 25 and 40 mb in the laboratory are presented in Figs 4–6. The conventional electrode $0,5 \times 4$ mm showed a plateau only at 5 mb suction. Both of the tip-point microelectrodes showed typical plateaus for all the suctions considered. Fig. 7 shows current-voltage relations for both tip-point microelectrodes at 21% of oxygen. As can be seen electrode *b* does not show a plateau at 90 mb suction, while for electrode *c* the plateau disappeared at 120 mb suction. This confirms the validity of the hypothesis that OH^- ions accumulation is responsible for the disappearance of the plateau in unsatu-

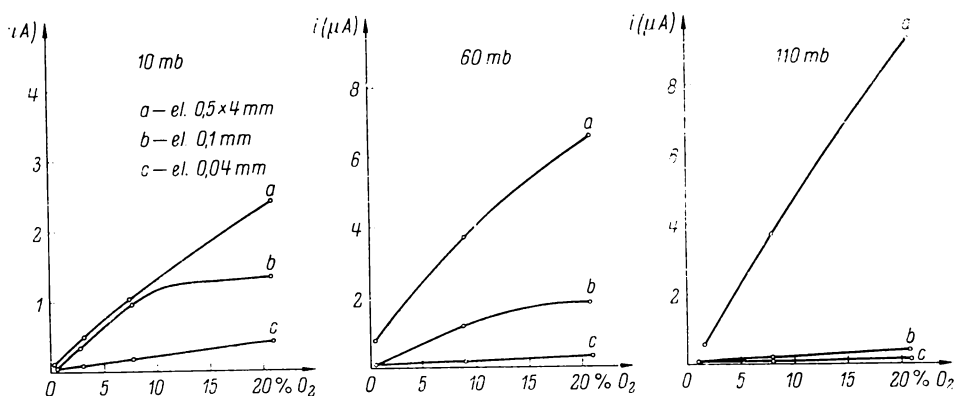


Fig. 8. Effect of oxygen content on measured current intensity at $-0,65$ V voltage for different suction values

rated soil and that this effect can be avoided by the construction of tip-point microelectrodes. The relationship of the measured current on oxygen concentration (Fig. 8) is linear for *a* and *c* electrodes, while for the *c* electrode this relationship is curvilinear at 21% O_2 . This means that activation polarisation due to an insufficient reaction rate on the electrode occurred in this case.

CONCLUSION

The investigations showed that the accumulation OH^- ions on the electrode surface is responsible for the disappearance of the polarographic plateau in unsaturated soils during measurements of ODR by

using conventional electrodes. Construction of the tip-point microelectrodes makes it possible to eliminate this at least for low suction range. It seems possible to widen this range by the construction of tip-point electrodes of further decreased surface of single platinum tips.

REFERENCES

- [1] Gawlik J., Malicki M., Stępniewski W. S.: The problem of effective voltage control in measurements of ODR in soil. *Pol. J. Soil Sci.* 1977, 10, 9-14.
- [2] Lemon E. R., Erickson A. E.: The measurement of oxygen diffusion in the soil with a platinum microelectrode. *Soil Sci. Soc. Am. Proc.* 1952, 16, 160-163.
- [3] Malicki M., Walczak R.: A gauge of the redox potential and the oxygen diffusion rate in the soil, with an automatic regulation of cathode potential. *Zesz. probl. Post. Nauk rol.* 1978, 220.
- [4] McIntyre D. S.: The platinum microelectrode method for soil aeration measurement. *Adv. Agrom.* 1970, 22, 235-283.

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ПРИГОДНОСТЬ ТОЧЕНОГО МИКРОЭЛЕКТРОДА ДЛЯ ИЗМЕРЕНИЙ ПОКАЗАТЕЛЯ ODR В ПОЧВЕ

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Резюме

Целью работ было установление поскольку затухание полярографического плато редукиции кислорода в измерениях ODR (Охуден Diffusion Rate) в насыщенных почвах обязано аккумуляции ионов OH на поверхности электрода и можно-ли этот эффект устанить путем конструкции точечных микроэлектродов с пониженным количеством выделяемых гидроксильных ионов OH.

Исследования заключались в сравнении зависимости тока от напряжения для трех типов электродов: конвенционного (обще принятого) с размерами 0,5×4 мм и двух точечных микроэлектродов сделанных из платиновой проволоки диаметром 0,1 и 0,04 мм. Характеристика действия электродов была проведена в условиях разных величин силы и концентрации кислорода в почвенном воздухе. Полученные результаты подтвердили, что отсутствие полярографического плато редукиции кислорода для платиновых электродов обычно применяемых в измерениях ODR является последствием неудовлетворительной скорости отвода гидроксильных ионов с поверхности электрода. Значительное уменьшение активной поверхности электрода устраняет этот эффект и предоставляет возможность получить плато, а следовательно и достоверное измерение ODR. При употреблении электрода сделанного из проволоки Φ 0,04 мм получено плато для чернозема в диапазоно 0-90 mb а для электрода из проволоки Φ 0,1 мм в диапазоне 0-40 mb. Следовательно по-прежнему диапазон измерения сильно ограничен и необходимо стремиться к его расширению путем применения проволоки еще

меньшего диаметра. Конструкция электрода должна подлежать изменению так, чтобы свести к минимуму физические эффекты вызываемые его вдавливанием в почву.

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PRZYDATNOŚĆ MIKROELEKTRODY PUNKTOWEJ DO POMIARÓW
WSKAŹNIKA ODR W GLEBIE

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Streszczenie

Celem pracy było stwierdzenie, czy zanik polarograficznego plateau redukcji tlenu przy pomiarach ODR w glebach nie nasyconych spowodowany jest akumulacją jonów OH na powierzchni elektrody i czy efekt ten można wyeliminować przez konstrukcję mikroelektrod punktowych o zmniejszonej ilości wydzielanych jonów hydroksylovych OH.

Badania polegały na porównaniu zależności natężenia prądu od napięcia dla trzech typów elektrod: konwencjonalnej o wymiarach $0,5 \times 4$ mm oraz dwu mikroelektrod punktowych wykonanych z drutu platynowego o średnicy 0,1 i 0,4 mm. Badania charakterystyk elektrod wykonano przy różnych wartościach ssania i przy różnych stężeniach tlenu w powietrzu glebowym. Uzyskane wyniki badań potwierdziły, że brak polarograficznego plateau redukcji tlenu dla elektrod platynowych stosowanych powszechnie w pomiarach ODR wynika z niewystarczającej prędkości odprowadzania jonów hydroksylovych z powierzchni elektrody. Znaczne zmniejszenie powierzchni czynnej elektrody eliminuje ten efekt i umożliwia uzyskanie plateau, a zatem wiarygodny pomiar ODR. Przy użyciu elektrody skonstruowanej z drutu 0,04 mm uzyskano plateau dla czarnoziemiu w zakresie 0–90 mb, a dla elektrody z drutu 0,1 mm — w zakresie 0–40 mb. Nadal więc zakres pomiarowy jest ograniczony i należy dążyć do jego dalszego rozszerzenia przez zastosowanie drutu o jeszcze mniejszym przekroju. Konstrukcja elektrody powinna ulec zmianie, tak aby zminimalizować efekty fizyczne spowodowane jej wciskaniem do gleby.

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