The meniscus cell — partially immersed gas-diffusion electrodes
Part II. Modelling

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Abstract

In this paper, a mathematical model and some of the difficulties in the attempts to apply this model in the meniscus-cell experiments are discussed. The model is derived under the assumption that no potential or electrolyte concentration gradients are present in the electrolyte-filled pores of the catalyst layer. A second assumption is that there are no potential gradients in the solid phase of the catalyst layer; this is the case when the current density is kept low.

Introduction

The gas-diffusion characteristics in the catalyst layer of a gas-diffusion electrode are of vital importance for the performance of the electrode. In many cases, transport resistance is the limiting factor in the electrode performance.

The initial idea of the meniscus method enabled to screen the gas-diffusion characteristics of electrode formulations in a cost-efficient manner. Later, it has been suggested that, may be, more information could be drawn from the results of the experiments with mathematical modelling. In order to emphasize the gas-diffusion resistance, the gas-diffusion path was made long by immersing the electrode into the electrolyte. To make the other resistances small, the current density was kept low in the experiments. The assumptions for the model were that the *IR* drop in the catalyst layer is equal to zero, and that there are no concentration gradients in the electrolyte phase inside the catalyst layer.

This paper describes the experiments, and discusses the results of the experiments.

Experimental

The electrodes were prepared by the rolling technique initially developed by Schautz [1] and Kordesch *et al.* [2], and then further developed by Kiros and Schwartz [3] at the Royal Institute of Technology and Kivisaari *et al.* [4] at the Helsinki University of Technology. The rolled electrode sheet was fastened on a support (nickel screen or nickel plate) by rolling and pressing.

The current–potential curves were measured by gradually immersing of the electrode into the electrolyte, 1 mm at the time up to 5 mm immersion (Fig. 1).

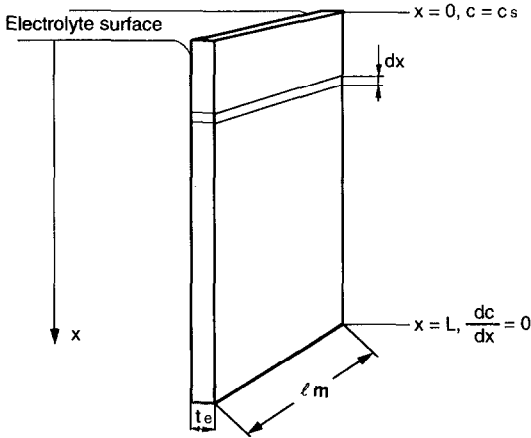The measurements were carried out in the same way as described in ref. 5.

Fig. 1. Electrode immersed in electrolyte to depth L.

Mathematical model [6]

$$i_s = -\sigma \operatorname{grad} V_s \tag{1}$$

$$i_l = -\kappa \operatorname{grad} V_l \tag{2}$$

$$\operatorname{div} i_l = -\operatorname{div} i_s = i_T \tag{3}$$

$$\operatorname{div}(-D_e \operatorname{grad} c) = \frac{i_T}{4F} \tag{4}$$

$$i_T = AcE \exp\left(\frac{V_l - V_s}{B}\right) = Tc \tag{5}$$

$$E = \left[\frac{\gamma}{\tanh \gamma} + \frac{tA \exp\left[\dfrac{V_l - V_s}{B}\right]}{D_1}\right]^{-1} \tag{6}$$

$$\gamma = \gamma_0 \exp\left[\frac{V_l - V_s}{2B}\right] \tag{7}$$

where,

A = coefficient in rate equation, A mol^{-1};

B = natural Tafel slope, V;

c = oxygen concentration in gas pores, mol m^{-3};

D_e = effective diffusivity of oxygen through the gas-pore system, m^2 s^{-1};

D_1 = diffusivity of oxygen dissolved in electrolyte, m^2 s^{-1};

E = effectiveness factor = reaction rate in electrolyte-flooded agglomerate region divided by the hypothetical reaction rate if the oxygen concentration were the same as in the interface between gas and electrolyte throughout the agglomerate region;

F = Faraday constant, A s mol^{-1};

i_T = transfer current per volume catalyst layer, A m^{-3};

t = thickness of the electrolyte film surrounding the electrolyte-flooded agglomerate regions, m;

$$T = AE \exp\left(\frac{V_1 - V_s}{B}\right)$$

V_1 = electric potential of a suitable oxygen-independent reference electrode in equilibrium with the electrolyte, V;
V_s = electric potential in the solid phase, V;
γ = Thiele modulus of the electrolyte-filled agglomerate regions, and
γ_0 = the value of the Thiele modulus at zero electrode potential.

In the meniscus cell case, with a large influence of oxygen-diffusion resistance in the gas-pore system and assuming a uniform electrode potential throughout the catalyst layer, it may be assumed the hypothesis that the electrode can be modelled completely by eqns. (4)–(7).

In this case, the reaction is a first-order irreversible reaction with pore diffusion. Equations (4)–(7) give the following solution:

$$-D_e \operatorname{div} \operatorname{grad} c = \frac{i_T}{4F} \tag{8}$$

$$\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) = -\frac{i_T}{4FD_e} \tag{9}$$

Applying eqn. (5) leads to a three-dimensional differential equation of second order:

$$\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) = \frac{T}{4FD_e} c \tag{10}$$

Since the oxygen concentration depends on the depth-of-immersion only, eqn. (10) can be written as:

$$\frac{d^2 c}{dx^2} - \frac{T}{4FD_e} c = 0 \tag{11}$$

Then eqn. (11) has the general solution:

$$c = M_1 \exp(mx) + M_2 \exp(-mx) \tag{12}$$

where,

$$m = \sqrt{\frac{T}{4FD_e}} \tag{13}$$

The coefficients M_1 and M_2 can be determined from the limiting conditions of the oxygen concentration at the electrolyte/gas interface and at the lower edge of the electrode:

$$c = c_s, x = 0$$

$$\frac{dc}{dx} = 0, x = L$$

$$M_1 = \frac{c_s \exp(-mL)}{\exp(mL) + \exp(-mL)} \tag{14}$$

$$M_2 = \frac{c_s \exp(mL)}{\exp(mL) + \exp(-mL)} \tag{15}$$

$$c = \frac{c_s \exp(-mL)}{\exp(mL) + \exp(-mL)} \exp(mx) + \frac{c_s \exp(mL)}{\exp(mL) + \exp(-mL)} \exp(-mx) \tag{16}$$

For a segment of height dx extended over the whole cross-sectional area of the catalyst layer the total current generated di_{tot} can be expressed by:

$$di_{tot} = -i_T t_e l_m \, dx = Tc(x) t_e l_m \, dx \tag{17}$$

where t_e and l_m denote the electrode thickness and the meniscus length, respectively, and for the total electrode:

$$i_{tot} = \int_0^L -i_T t_e l_m \, dx = T t_e l_m \int_0^L c(x) \, dx \tag{18}$$

and according to eqn. (16) the total current can be expressed in terms of the depth-of-immersion (L):

$$c(x) = \frac{c_s \exp(-mL)}{\exp(mL) + \exp(-mL)} \exp(mx) + \frac{c_s \exp(mL)}{\exp(mL) + \exp(-mL)} \exp(-mx) \tag{19}$$

$$i_{tot} = T t_e l_m \int_0^L \left(\frac{c_s \exp(-mL)}{\exp(mL) + \exp(-mL)} \exp(mx) + \frac{c_s \exp(mL)}{\exp(mL) + \exp(-mL)} \exp(-mx) \right) dx \tag{20}$$

integration and rearranging gives:

$$i_{tot} = T t_e l_m \frac{c_s}{m} \tanh(mL) \tag{21}$$

From eqn. (21) it can be seen that i_{tot} is proportional to c_s and should be five times larger if the oxygen concentration is five times higher.

The curves in Fig. 2 are calculated by adjusting the unknown parameters D_e, γ_0, A and B so that the calculated curves fit with the experimental data.

In the modelling of the curves in Fig. 2, the film thickness, t, was set to zero.

Results and discussion

Most surprising was that the results of the modelling agree with the experimental results when they are not supposed to, and that they are not in agreement when they should be.

Variation of current with depth of immersion

Nickel screen — whole electrode — immersion

The results obtained from the experiments could fairly well be described with the model given in Fig. 2. Although the results from the experiments and the model
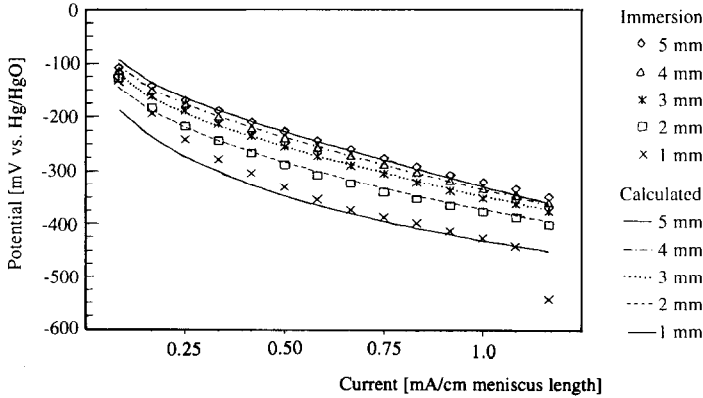
Fig. 2. Current–voltage curve for electrode on nickel screen; meniscus experiment 74128; electrode 74122 with Shawinigan, 37% PTFE, and silver as catalyst.
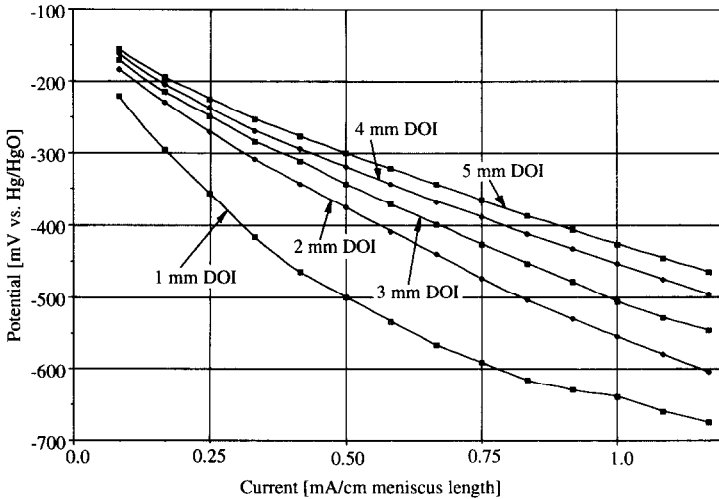

Fig. 3. Current–voltage curve for electrode on nickel plate immersion; meniscus experiment 74114; electrode 74104 with Shawinigan, 40% PTFE, and silver catalyst. DOI = depth-of-immersion.

are in accordance with each other, this may be a coincidence since the part of the electrode which is above the electrolyte surface may be electrochemically active. This is the case if the electrolyte is penetrating inside the electrode due to capillary forces. The second reason is that the catalyst layer prepared on a nickel screen will not be of the same shape as the catalyst layer in a real electrode, cf., Fig. 6 in ref. 5.

Nickel plate — whole electrode — immersion
    In this case (Fig. 3), the problem with the irregularity in the thickness of the catalyst layer was eliminated. The problem of the electrolyte penetrating inside the electrode matrix was not solved in this case.

Nickel plate — strip electrode — cutting

In this case (Fig. 4), both the problem with irregular thickness and the electrolyte penetrating due to capillary forces in the catalyst layer matrix are eliminated. The odd behaviour of the results of these experiments indicates some kind of uncontrolled process or processes going on; one of these processes could be a convection in the electrolyte, and that this convection contributes to the transport of oxygen to the lower parts of the electrode, but this is not a suitable explanation to the phenomena observed (see Fig. 5). The assumption in the model is that the diffusion of oxygen through the bulk of the electrolyte can be neglected. If there is a convection stream, oxygen can be transported down to the bulk, and reacts on the electrode surface.

Nickel plate — strip electrode with convection inhibitor — cutting

In this test, an attempt was made to eliminate possible convection, achieved by placing a pocket of non-woven polypropylene cloth around the strip of catalyst layer.
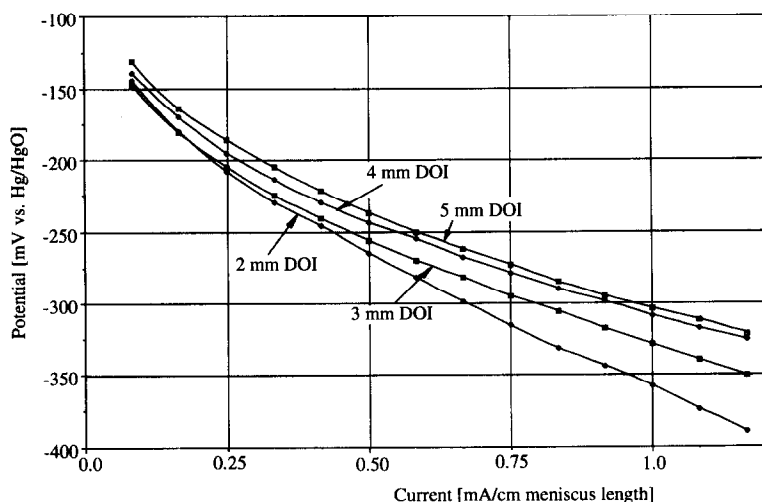

Fig. 4. Current–voltage curve for 'strip' electrode on nickel plate-cutting; meniscus experiment 74134; electrode 74125 with Shawinigan, 30% PTFE, and silver catalyst. DOI = depth-of-immersion.
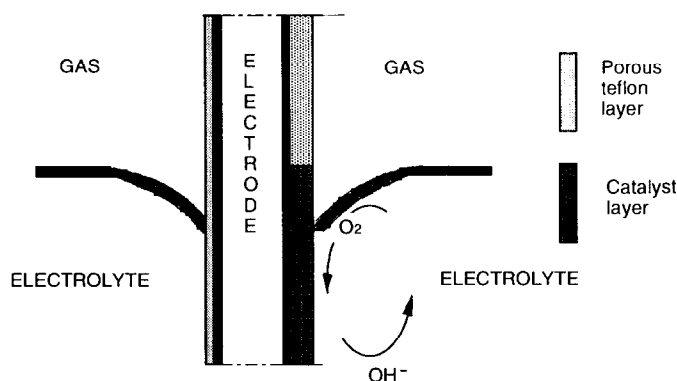

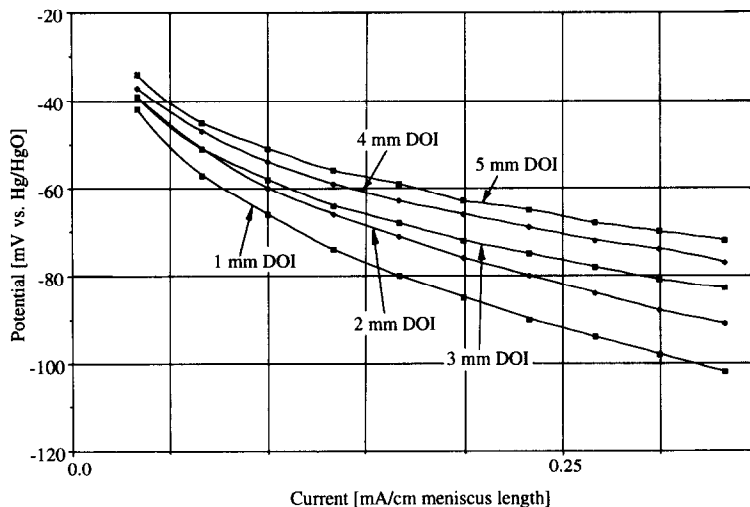Fig. 5. Possible convection in electrolyte.

Fig. 6. Current–voltage curve for 'strip' electrode on nickel plate-cutting, pocket; meniscus experiment 910617; electrode 910111 with Vulcan, 30% PTFE, and CoTMPP catalyst. DOI = depth-of-immersion.

As can be seen in Fig. 6, the curves measured became much more regular, but still there may be *iR* drop and concentration gradients affecting the result, as the experiments cannot be described with the model. With the pocket of non-woven polypropylene cloth, the convection phenomena were reduced, but, at the same time, it gave rise to other problems — i.e., an *iR* drop > 0 and concentration gradients in the electrolyte phase of the electrode. One problem was that the non-woven pocket lost its elasticity when it was immersed in the electrolyte. This problem was solved by replacing the pocket with a new one, every time the electrode was cut.

In order to find out if large electrolyte gradients were formed in the electrode during measurement, a normal run [5] was made, but instead of shutting off the current a 'return' measurement was done by decreasing the current stepwise and obtaining another curve. The distance between the curves, Fig. 7, indicates that the formation of electrolyte gradients in the electrode is not a too big problem.

Variation of current with oxygen concentration

One of the assumptions for the model is that there are no *IR* drops in the half-cell. The current density has to be kept low in order to keep a uniform electrode potential in the catalyst layer.

An experiment was carried out, using different gas mixtures, to find out if *IR* drops were formed. According to the model the current generated when running the electrode on 100% oxygen should be five times greater than when the electrode is run on a mixture of 20% oxygen in nitrogen (air). The results of such measurements are shown in Fig. 8. The curves in Fig. 8 show that the results of this measurement do not follow the model. The factor between 100 and 20% oxygen is only 4.25 at 5 mm immersion and −48 mV versus Hg/HgO. At −62 mV the factor is 3.77. The difference between 20 and 1% oxygen in nitrogen should be 20 if the electrode follows
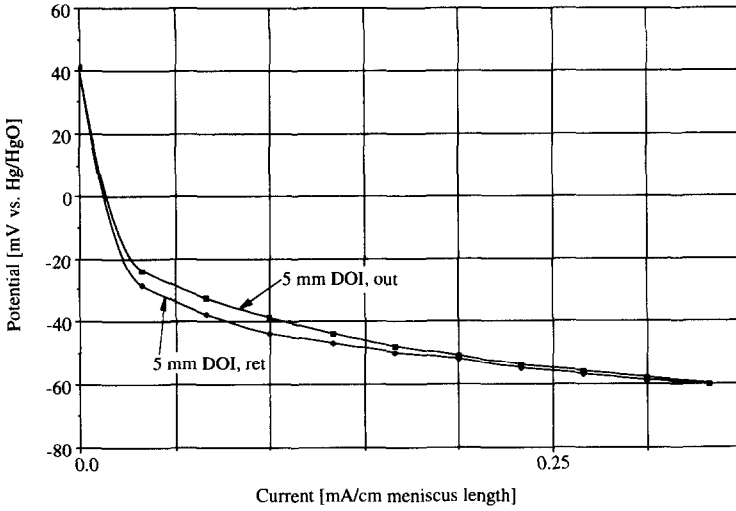
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Fig. 7. Current–voltage curve for 'strip' electrode on nickel plate-cutting, pocket, hysteresis experiment 910701; electrode 910111 with Vulcan, 30% PTFE, and CoTMPP catalyst. DOI = depth-of-immersion.
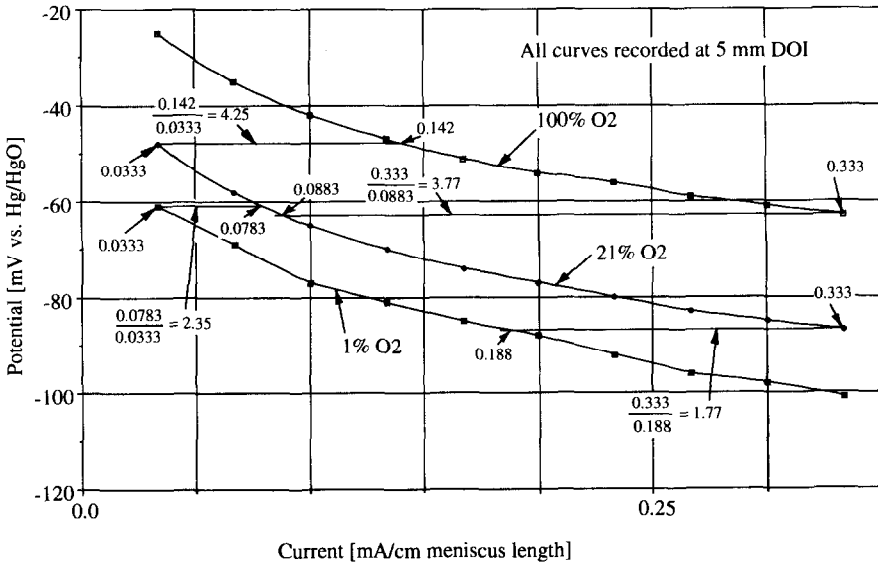

Fig. 8. Current–voltage curve for 'strip' electrode on nickel plate-cutting, pocket, different gas mixtures 910625; electrode 910111 with Vulcan, 30% PTFE, and CoTMPP catalyst. DOI = depth-of-immersion.

the model. In this experiment the factor is 2.35 at −60 mV versus Hg/HgO and 1.77 at −86 mV. This indicates that there is an ohmic contribution to the overall polarization.

Non-wetting and potential gradient in the electrolyte phase

One of the problems was to get the catalyst layer wetted enough. If the layer is too dry, the ionic conductivity of the catalyst layer will be poor, and the ohmic losses will be great. Below, some rough calculations are made to exemplify how the ohmic losses are influenced by a change in conductivity in the catalyst layer.

An attempt to control this factor was made by immersing the electrode in the electrolyte and taking it out after some time, weighing it and then immersing it again. This procedure was repeated until the weight of the electrode did not increase anymore. The results of these experiments showed that the electrode was saturated with electrolyte after 4 to 5 h.

Consider a slab, with height 1 mm, width 60 mm and thickness 0.4 mm, of the catalyst layer (Fig. 9). This gives an area of 0.6 cm^2. Let the current be 6.0 mA $\Rightarrow$ 10 mA/cm^2, then:

$$i = \frac{x}{\Delta x} i_{max} = -\kappa \frac{dU}{dx} \tag{22}$$

$$x \, dx = -\frac{\kappa \Delta x}{i_{max}} \, dU \tag{23}$$

$$\frac{(\Delta x)^2}{2} = \frac{\kappa \Delta x \Delta U}{|i_{max}|} \tag{24}$$

$$\Delta U = \frac{|i_{max}| \Delta x}{2\kappa} = \frac{10 \times 0.04 (\text{mA cm}^{-2} \text{ cm})}{2\kappa [\text{mA mV}^{-1} \text{ cm}^{-1}]} = \frac{0.4}{2\kappa} \text{ (mV)} \tag{25}$$

Free electrolyte: $\kappa \approx 1.0 \ (\Omega^{-1} \text{ cm}^{-1}) \Longrightarrow \Delta U \approx 0.20$ mV

Normal layer: $\kappa \approx 0.01 \ (\Omega^{-1} \text{ cm}^{-1}) \Longrightarrow \Delta U \approx 20.0$ mV

Dry layer: $\kappa \approx 0.001 \ (\Omega^{-1} \text{ cm}^{-1}) \Longrightarrow \Delta U \approx 200$ mV

$\kappa = $ conductivity

From these rough calculations, the impact of non-wetting on the current–voltage curves can be seen. For a normal layer the contribution is about 20 mV. This figure gives an error of $\sim 10\%$ for the larger polarizations. For dry layers, the voltage drop due to low conductivity gives a considerable contribution to the overall polarization. If the catalyst layer is wet enough [7] the IR contribution could be neglected, at least in the absence of the polypropylene pocket (see above).
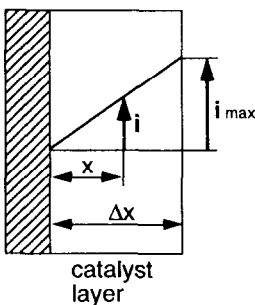

Fig. 9. Electrical conductivity in catalyst layer.

Conclusions

1. After a first glance at the results with electrodes on a nickel mesh, the model seems to predict the current–voltage curves pretty well. The curves were calculated by fitting parameters to the experimental data.

2. Due to difficulties in the experiment (discussed above) it was not possible to predict the current–voltage curves for the other experiments with the model.

3. The difficulties in the experiment were larger than it was assumed in the beginning.

4. Attempts to eliminate one uncontrolled factor often gave rise to new uncontrolled factors, i.e., iR drop and concentration gradients with the polypropylene pocket.

5. The hysteresis experiment implies that the polarization due to concentration gradients in the electrolyte could be neglected, even with the polypropylene pocket, but at the same time the danger for iR drop increases.

6. The effort to carry out an experiment, with all the factors controlled, was not successful in this study.

Acknowledgement

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