

Discussion

Comment on “A one dimensional model of a methanol fuel cell anode”  
[K. Scott, P. Argyropoulos, J. Power Sources 137 (2004) 228]

A.A. Kulikovsky<sup>\*,1</sup>

Research Center “Juelich”, Institute for Materials and Processes in Energy Systems (IWV-3), D-52428 Juelich, Germany

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The paper by Scott and Argyropoulos deals with the analytical model of the anode side of a direct methanol fuel cell (DMFC). The authors consider two expressions for the rate of methanol oxidation  $j$

$$j = \frac{6Fk_{10}C_M \exp(\beta\eta)}{1 + k_{20}C_M \exp(\beta\eta)} \quad (16)$$

and

$$j = \frac{6Fk_{10}C_M \exp(\beta\eta)}{C_M + k_{20} \exp(\beta\eta)}, \quad (22)$$

which correspond to the two alternative reaction pathways (equation numbers are those in [1]). Here  $\eta$  is local overpotential; for the other designations see [1].

Expressions (16) and (22) are then used to calculate the profile of proton current density (denoted also as  $j$ ) across the anode catalyst layer. In [1], this problem is formulated as follows (p. 232): “In the catalyst region, the change in ionic current density, i.e. due to proton conductivity is given by

$$\frac{dj}{dx} = -aj \quad (33)$$

where,  $a$ , is a specific reaction surface area ( $\text{m}^{-1}$ ).” Linear relation (33) between  $j$  and  $dj/dx$  greatly simplifies solution of the problem [1]. Unfortunately, Eq. (33) is erroneous.

Eqs. (16) and (22) determine the rate of methanol oxidation reaction. Although  $j$  in (16) and (22) has dimension

$\text{A cm}^{-2}$ , this value is *not* a local current density, but the rate of charge production per unit area of the catalyst surface per second. Physically,  $j$  on the right side of (33) is a scalar.

In contrast, the left side of (33) should contain proton current density, which is a vector. The main reason for the subsequent errors in [1] stems from the mixing of these two different values, which are designated by the same symbol  $j$  in Eq. (33).

Let proton current density is  $i$ ; the change in  $i$  with the distance  $x$  across the catalyst layer is due to the protons generated in electrochemical reaction.<sup>2</sup> Eq. (33), therefore, should be

$$\frac{di}{dx} = -aj \quad (33a)$$

where  $j$  is given by (16) or (22), depending on the model of reaction kinetics. Note that no linear relation between  $i$  and  $di/dx$  exists. Eq. (33a) and the Ohm’s law  $i = -\sigma(d\eta/dx)$  form a system of two equations for two variables:  $i(x)$  and  $\eta(x)$ .<sup>3</sup> Accurate solution to this system for the case of  $j$  (22) is given in [2].

References

- [1] K. Scott, P. Argyropoulos, J. Power Sources 137 (2004) 228.
- [2] A.A. Kulikovsky, Electrochem. Commun. 5 (2003) 530.

\* Tel.: +49 2461 615396; fax: +49 2461 616695.

<sup>1</sup> On leave from Moscow State University, Research Computing Center, 199992 Moscow, Russia.

<sup>2</sup> Not “due to proton conductivity”, as stated in [1].

<sup>3</sup> Eq. (33) describes exponential profile  $j(x) = j_0 \exp(-ax)$  and no other equations are then required “to solve” the problem.