

Comment on “Out-of-Cell Oxygen Diffusivity Evaluation in Lithium–Air Batteries” by He et al.

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In a recent paper, He et al. (*ChemElectroChem* 2014, 1, 2052–2057) described a methodology for measuring out-of-cell oxygen diffusivity in lithium–air battery (LAB) cathodes, combining an electrochemical device with a classical gas-transport model. We will demonstrate here that the authors erroneously assumed that the Knudsen diffusivity of gaseous oxygen in the

porous cathode is smaller than the diffusivity in the electrolyte and, consequently, that the oxygen mass transport would limit the current output of the battery. Therefore, it is impossible to determine the oxygen diffusivity in LAB cathodes by using the electrochemical device proposed by the authors, comprising an oxygen pump, the LAB cathode, and an oxygen sensor.

Recently, He et al.^[1] reported an out-of-cell oxygen diffusivity evaluation of the porous cathode of Li–air batteries (LABs). The authors claimed that the proposed electrochemical device allows efficient and low-cost measurement of the oxygen diffusivity and other important battery parameters, such as electrode porosity, thickness, and tortuosity, as compared to previous methods that require multiple voltage–current experiments over an intact LAB. We will show that this claim is supported on an erroneous assumption and, consequently, the proposed electrochemical device proposed is unable to provide reliable oxygen diffusivity and other parameters of the porous cathode.

The electrochemical device described by He et al.^[1] is illustrated in Figure 1, which is identical to that shown in Figure 1a of that article. It comprises a LAB, which the authors refer to as

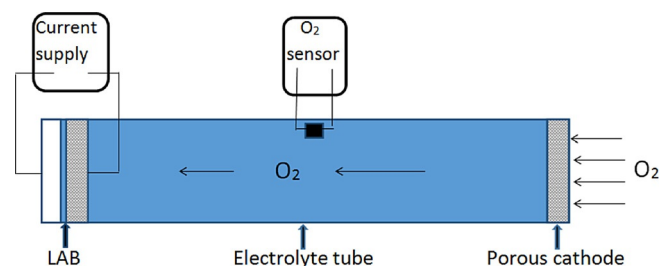


Figure 1. Electrochemical device to determine cathode oxygen diffusivity in LAB according to Ref. [1].

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an “oxygen pump”, that is, a component that consumes the oxygen that diffuses through the electrolyte tube, the porous disc (they called it the “cathode”, but it should be noted that it is not connected to any power supply and it is not part of the oxygen pump, i.e. it is a purely passive component) with microscale thickness, and an oxygen sensor located in between the porous “cathode” and the LAB.

Indeed, the authors proposed two devices, but the second one is essentially the same as that depicted in Figure 1 with a porous disc supporting the thin porous cathode, without modifying the basis of the proposed method.

The authors include a current supply to the oxygen pump, whose function is not clear, because the oxygen consumption is the spontaneous process in the LAB. Polarizing the LAB, in the way of increasing the amount of oxygen reduced in the LAB to form Li_2O_2 , would not be effective because the current will be limited by the amount of oxygen reaching the cathode of the LAB.

The oxygen sensor, whose principle of working is not described by He et al.,^[1] apparently would generate an electrical potential depending on the oxygen partial pressure inside the tube through the Nernst equation [Eq. (1) of Ref. [1]]. A similar setup was used by He et al.^[3] to measure H_2 – H_2O effective binary diffusivity in the porous anode of a solid oxide fuel cell (SOFC), probably inspired in the work by Zhao et al.,^[2] who used an oxygen sensor based on the oxygen-ion-conducting yttria-stabilized zirconia (YSZ) material to determine the effective diffusivity of O_2 – N_2 in a porous cathode of a SOFC at high temperatures (650–800 °C).

The setup of Figure 1 is proposed for determining the oxygen diffusivity of LAB cathodes based on the assumption that “the Knudsen diffusivity of the cathode is smaller than the oxygen diffusivity in the electrolyte”.^[1]

He et al.^[1] quoted that they calculated the effective Knudsen diffusion coefficient of oxygen in the porous cathode, by resorting to Equation (1):^[2]

$$D_{\text{O}_2}^{\text{eff}} = \frac{\varepsilon d}{3\tau} \left(\frac{8k_B T}{\pi m_{\text{O}_2}} \right)^{1/2} \quad (1)$$

where ε is the cathode porosity, τ the cathode tortuosity, d is the pore diameter, m_{O_2} is the molecular weight of oxygen, and k_{B} the Boltzmann constant. This is justified by the fact that the mean-free path of oxygen at ambient pressure is larger than the pore size.

Numerical values for $D_{\text{O}_2}^{\text{eff}}$ are not reported by He et al.,^[1] but it would be useful to estimate them for realistic structural parameters of LAB porous cathodes. For pores that are 10 and 50 nm in diameter, the oxygen Knudsen coefficients are 0.015 and 0.074 cm^2s^{-1} , respectively (for $\varepsilon=1$ and $\tau=1$). If realistic cathode parameters are $\varepsilon=0.5$ and $\tau=5$, the effective oxygen Knudsen diffusivity will be a factor of 10 smaller. Thus, it is highly improbable to find diffusion coefficients lower than $10^{-3} \text{cm}^2\text{s}^{-1}$ for oxygen in LAB cathodes assuming, as the authors did, that the pores are not embedded by the electrolyte.

The diffusion coefficient of oxygen in the electrolyte was estimated by He et al.^[1] by using the Stokes–Einstein equation [Eq. (2)]:^[4]

$$D_{\text{O}_2}^* = \frac{k_{\text{B}}T}{6\pi\eta r} \quad (2)$$

where η is the dynamic viscosity of the solvent and r is the hydrodynamic radius of oxygen. He et al.^[1] have not reported numerical values for this transport coefficient in order to compare with the oxygen diffusivity in the pores of the cathode, but they adopted $r=0.21 \text{ nm}$ and $\eta=0.02 \text{ cP}$ (1 cP = 1 mPa s) as a typical viscosity of the solvent. This hydrodynamic radius of oxygen is reasonable considering that the Lennard–Jones radius for oxygen is 0.173 nm,^[4] but the viscosity they used in the calculation is around a factor of 100 lower than the viscosity of a typical solvent for LAB (for instance, $\eta=1.99 \text{ cP}$ for DMSO at 25 °C). Indeed, the liquid-state diffusion coefficient of oxygen is $4.0 \cdot 10^{-6} \text{ cm}^2\text{s}^{-1}$, calculated for a viscosity of 2.59 cP, corresponding to 1 M LiPF₆ in PC:DME (1:1).

The authors did not justify the use of such an unusual value for the solvent viscosity in their calculation. However, even using such a low solvent viscosity, the diffusion coefficient of oxygen in the liquid will be around $5 \cdot 10^{-4} \text{ cm}^2\text{s}^{-1}$, which is much lower than the Knudsen diffusion in the gas phase ($7.4 \cdot 10^{-3} \text{ cm}^2\text{s}^{-1}$ for a porous cathode with $\varepsilon/\tau=0.1$).

In summary, a typical gas-state oxygen diffusion coefficient in the porous cathode should be around three orders of magnitude larger than the liquid-state value. Thus, their claim that “the electrochemical operation of the lithium–air battery is limited by the mass transport associated with cathode gas diffusion”^[1] is wrong. In support of their hypothesis, He et al.^[1] refer to a study by McCloskey et al.^[5] on the effect of electrocatalysts on the evolution oxygen reaction (OER) in LABs. In that work, it is concluded that the formation of an insoluble and immobile species (Li₂O₂) on the cathode surface precludes transport of species to active catalytic sites, making conventional OER electrocatalysis in a LAB implausible. That is, the analysis by McCloskey et al.^[5] does not support limited oxygen diffusivity in the cathode of a LAB, but only points out that the formation of solid products in the cathode during the discharge process diminishes the oxygen transport.

In addition, it is worthy to emphasize that oxygen transport in the cathode of a LAB barely takes place through completely electrolyte-free pores. Indeed, it is possible to distinguish cathodes that are flooded or partially flooded,^[6–8] and LAB cathodes that are flooded with solid deposit (Li₂O₂),^[9,10] but He and co-workers^[11] proposed recently a wetted model of a porous LAB cathode. In this model, a film of electrolyte covered the pore surface in such a way that both gas and liquid-oxygen diffusion should be considered.

Figure 2 shows the oxygen partial pressure profile (dashed lines) that would result according to the assumption by He et al.,^[1] as compared to the more realistic one (full lines), considering that the diffusion in the electrolyte is slower than the Knudsen diffusion in the pores.

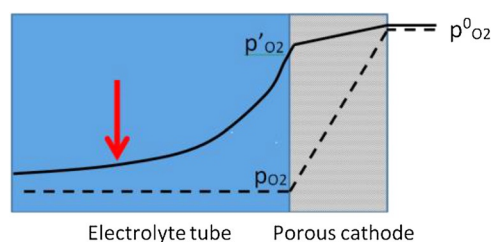


Figure 2. Oxygen partial pressure profiles in the setup proposed by He et al.,^[1] assuming cathode-limited diffusivity (dashed lines) or electrolyte-limited diffusivity (full lines). The arrow indicates an arbitrary position of the oxygen sensor in the tube.

The oxygen pressure gradients in Figure 2 are schematic, but clearly show that, under the assumption of cathode-limited diffusivity,^[1] the oxygen sensor would measure a low partial pressure, almost independent of its position in the electrolyte tube. The oxygen pressure in the tube will depend on the consumption of oxygen in the LAB, which, in this setup, works under flooded cathode conditions with slow oxygen transport. Therefore, the LAB should be polarized for enhancing oxygen reduction (discharge mode), and the oxygen partial pressure in the electrolyte tube will decrease to zero.

Under real conditions, that is, electrolyte-limited oxygen diffusivity, the oxygen partial pressure decays in the electrolyte tube, and now the oxygen sensor output will be dependent of its position. The discussion on the LAB operation conditions are also valid in this case, meaning that the use of a LAB as an oxygen scavenger in the setup proposed by He et al.^[1] is unappropiated. The depletion of oxygen to drive a stationary flux through the porous sample should be performed by an electrochemical cell without oxygen transport limitation; for instance, the formation of HgO on mercury is a good option.

Finally, it is important to discuss the relationship used by He et al.^[1] to obtain the effective oxygen diffusion coefficient, $D_{\text{O}_2}^{\text{eff}}$, from the measured (using the oxygen sensor) oxygen partial pressure in the tube, p_i and the applied current density, i , (using the power supply), that is, Equation (3):

$$p_i = p_0 - \left(\frac{p - p_0}{p} \right) \left[\frac{iRTI}{2FD_{\text{O}_2}^{\text{eff}}} \right] \quad (3)$$

where $p_0 = 0.21$ atm is the oxygen partial pressure in the cathode entrance, p is the total pressure (1 atm), l is the thickness of the porous cathode, R is the ideal gas constant, F is the Faraday constant, and T is the temperature.

This equation was derived by Zhao et al.^[2] by using the dusty gas model, as mentioned above, to determine the effective diffusivity of O_2 - N_2 in a porous cathode of SOFCs at high temperatures. The dusty gas model treats the solid part of the porous sample as an additional gaseous species with enormous mass, so that it is effectively immobile.

The transport equations for N_2 and O_2 , through the porous Sr-doped $LaMnO_3$ disc, correspond to an oxygen partial pressure gradient similar to that represented by the dashed line in Figure 2, because, in this case, the tube between the oxygen pump and the porous sample does not contain a liquid. Thus, the diffusion of oxygen in the tube occurs in the gaseous state and, consequently, its diffusivity is much larger than in the porous disc, a situation that is not valid for the device with the tube filled up with electrolyte, as shown in Figure 1.

Equation (3) is valid in the device proposed by He et al.^[1] if the oxygen pressure is measured in the interphase between the porous cathode and the electrolyte. Figure 2 shows that this pressure, p'_i is different from that measured in the oxygen sensor position. Moreover, in the conditions of the experiment, it is plausible that the liquid electrolyte partially penetrates the pores by capillarity, and the boundary conditions employed to derived Equation (3) are not longer valid.

We conclude that the electrochemical device proposed by He et al.^[1] to determine oxygen diffusivity in a LAB porous cathode is not viable, because it is based on an incorrect assumption. The diffusivity of oxygen in the electrolyte is larger than in the porous cathode, and then the oxygen partial pressure in the tube will depend on the sensor location. An additional problem that could emerge, if the device is handled as described, is the use of a LAB as oxygen pump, as the flow of oxygen at the flooded LAB cathode will be very low.

The evaluation of the effective diffusion coefficient of oxygen in a dry porous cathode could be achieved with the electrochemical device described by Zhao et al.,^[2] as shown in Figure 3, provided that the distance between the sample and the high-temperature couple YSZ oxygen pump/oxygen sensor is long enough to avoid errors due to thermal gradients.

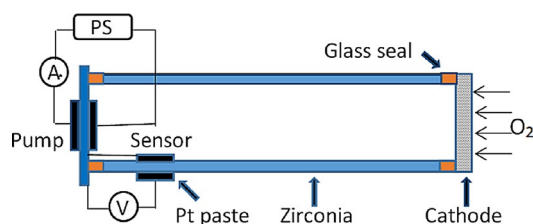


Figure 3. Electrochemical device for measuring the diffusivity in dry cathodes using a high-temperature sensor and oxygen pump (see details in Ref. [2]).

A simpler device could be developed by resorting to a low-temperature oxygen pump and sensor, as shown in Figure 4. A Clark electrode with a platinum sensing electrode and a silver reference electrode, enclosed within an oxygen-permeable membrane, could be an adequate sensor for this purpose,^[12] whereas a second porous sample with known diffusivity and in contact with a controlled oxygen partial pressure recirculating stream could act as an oxygen pump.

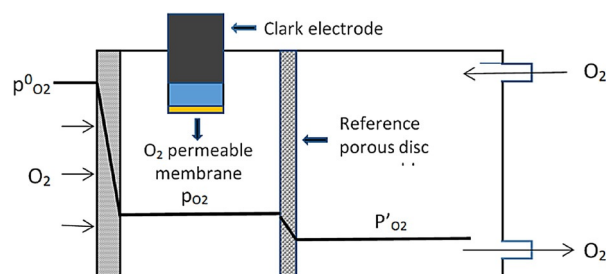


Figure 4. A possible device for measuring oxygen diffusivity in dry cathodes of LABs.

Alternatively, the oxygen diffusivity of a porous cathode in contact with air on one side, and electrolyte on the other side, can be determined by resorting to the Clark electrode immersed in the electrolyte. In this case, instead of forcing a stationary flow with an oxygen pump, the non-stationary flow can be followed by measuring the oxygen concentration as a function of time and distance to the cathode/electrolyte interphase, using an appropriate geometry to solve the non-stationary diffusion equation.¹

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¹ The authors of *ChemElectroChem* **2014**, *1*, 2052–2057 declined to reply to this comment.

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