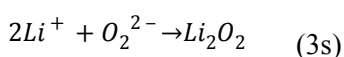
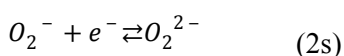
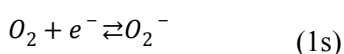


## SUPPLEMENTARY MATERIAL

### 1. The rate law equation for the oxygen reduction reaction

One of the primary goals of this study was to relate the structure of the ionic liquid's cation to the rate constant for electron transfer reaction at the cathode. The overall rate constant at the cathode can be obtained from the electron transfer rate constants of the individual intermediate reactions. The reduction reactions followed by lithium peroxide salt formation are as follows:



According to the third reaction, the production rate of  $Li_2O_2$  can be written as:

$$\frac{d[Li_2O_2]}{dt} = k_3[Li^+]^2[O_2^{2-}] \quad (4s)$$

Assuming that the formation of lithium peroxide from its constituent ions happens relatively fast compared to the electron transfer reactions based on steady state approximation, superoxide and peroxide ions will be the intermediate species with constant concentration over time:

$$\frac{d[O_2^-]}{dt} = 0 \rightarrow k_1[O_2] - k_{-1}[O_2^-] - k_2[O_2^-] + k_{-2}[O_2^{2-}] = 0 \quad (5s)$$

Therefore, it follows that the concentration of superoxide ion can be expressed as:

$$[O_2^-] = \frac{k_1[O_2] + k_{-2}[O_2^{2-}]}{k_{-1} + k_2} \quad (6s)$$

Also, according to the aforementioned steady state approximation, the rate of change of concentration of peroxide ion is assumed to be negligible, which yields:

$$\frac{d[O_2^{2-}]}{dt} = 0 \rightarrow k_2[O_2^-] - k_{-2}[O_2^{2-}] - k_3[Li^+]^2[O_2^{2-}] = 0 \quad (7s)$$

Therefore, the concentration of peroxide ion is obtained from Eq. (8s):

$$[O_2^{2-}] = \frac{k_2[O_2^-]}{k_{-2} + k_3[Li^+]^2} \quad (8s)$$

By combining Eq. (6s) and Eq. (8s):

$$[O_2^{2-}] = \frac{k_2}{k_{-2} + k_3[Li^+]^2} \left( \frac{k_1[O_2] + k_{-2}[O_2^{2-}]}{k_{-1} + k_2} \right) \quad (9s)$$

Therefore, the concentration of peroxide ion can be written in a simplified form as:

$$[O_2^{2-}] = \frac{k_1 k_2 [O_2]}{k_3 [Li^+]^2 (k_{-1} + k_2) + k_{-1} k_{-2}} \quad (10s)$$

By substituting Eq. (10s) into Eq. (4s), the rate law of the  $Li_2O_2$  production is obtained as:

$$\frac{d[Li_2O_2]}{dt} = k_3 [Li^+]^2 \left( \frac{k_1 k_2 [O_2]}{k_3 [Li^+]^2 (k_{-1} + k_2) + k_{-1} k_{-2}} \right) \quad (11s)$$

According to the calculated values for the forward and backward electron transfer rate constants, since  $k_{-1}$  and  $k_{-2}$  have very small values while  $k_2$  and  $k_3$  are very large, we can write:

$$k_3 [Li^+]^2 (k_{-1} + k_2) \gg k_{-1} k_{-2} \quad (12s)$$

Therefore, we can simplify Eq. (11s) to Eq. (13s):

$$\frac{d[Li_2O_2]}{dt} = \left( \frac{k_1 k_2}{k_{-1} + k_2} \right) [O_2] = k_{et(tot)} [O_2] \quad (13s)$$

Finally the overall electron transfer reaction rate constant can be written as:

$$k_{et}(tot) = \left( \frac{k_1 k_2}{k_{-1} + k_2} \right) \quad (14s)$$

This overall rate constant for the electron transfer reactions has been calculated and analyzed in the current study.

## 2. Zero-point energy

Quantitative information on zero point energy for all the species involved in the electrochemical reduction of oxygen into superoxide and peroxide ions is provided in Table 1s.

**Table 1s.** The zero-point energies of the species involved in the oxygen reduction reaction are provided.

Species	Charge	Zero-Point Energy (kJ.mol <sup>-1</sup> )
Oxygen	0	9.762472139
	-1	10.62024929
Superoxide	0	5.788149742
	-1	7.033665079
	-2	6.028976766
Peroxide	-1	3.079278690
	-2	4.080583737

## 3. Cross checking calculation with higher level of theory

The geometry optimization and energy calculation for neutral oxygen molecule was done with MP2 level of theory as well. As shown in the table below, the difference is less than 1.5%. Therefore, the rest of calculation was done using B3LYP with 6-311++G\*\* as the basis set in order to reduce the computational time.

**Table 2s.** The O-O distance in the optimized structure of neutral oxygen as well as the total energy from calculations at the MP2 and B3LYP level of theory are provided.

Neutral Oxygen		
Level of Theory	O-O Distance	Total Energy (Hartree)
MP2	0.61199788	-150.0791332
B3LYP, 6-311++G**	0.60308591	-150.3720950
<b>% Difference</b>	<b>1.46%</b>	<b>-0.20%</b>