Supporting information

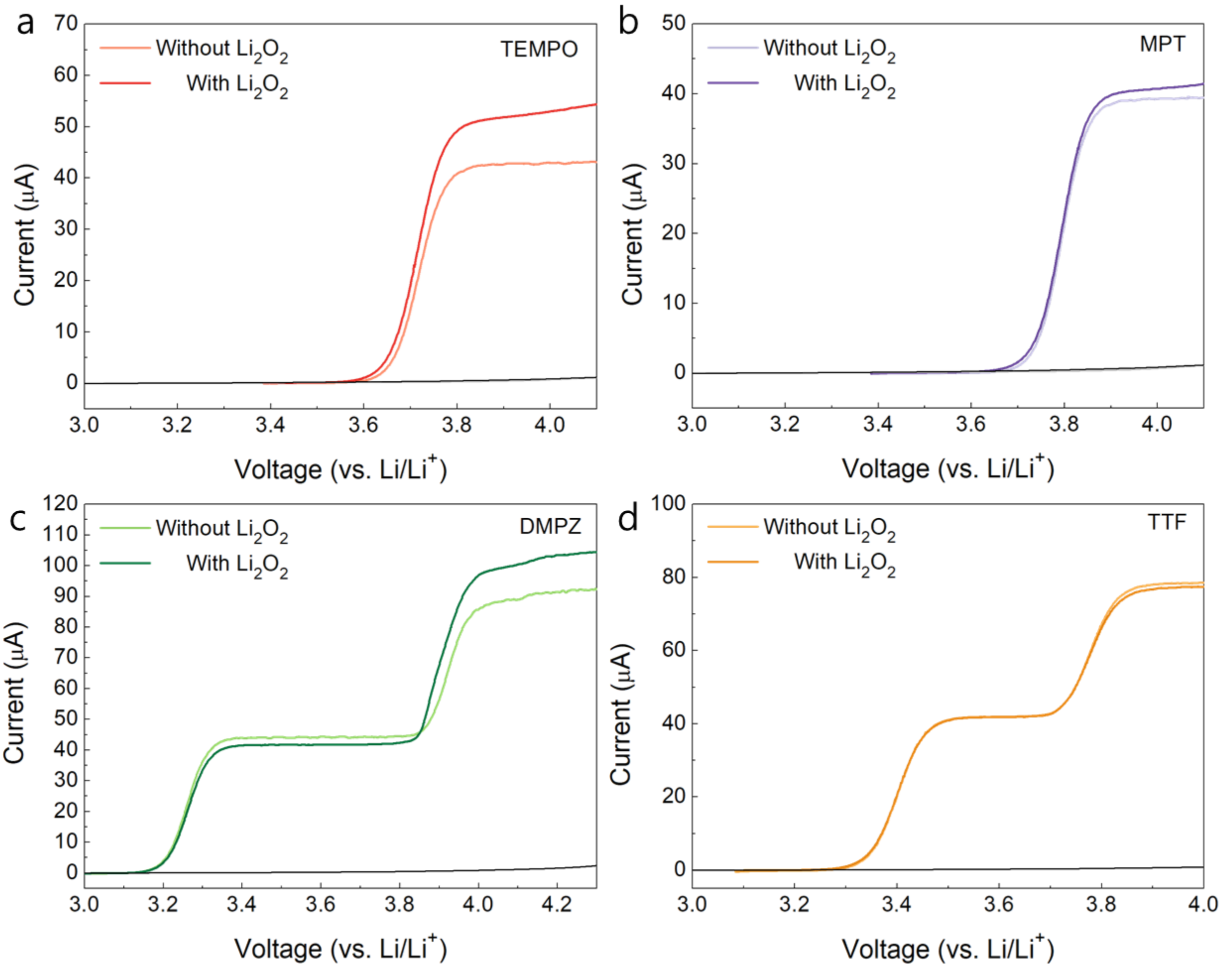

Figure S1. LSV profiles with RDE of TEMPO (a), MPT (b), DMPZ (c), and TTF (d). All the voltage scans were conducted at a scan rate of 1 mV s^{-1} using 1 M LiTFSI in DME containing 1 mM of the RM and 30 mM of dispersed Li_2O_2 powder.

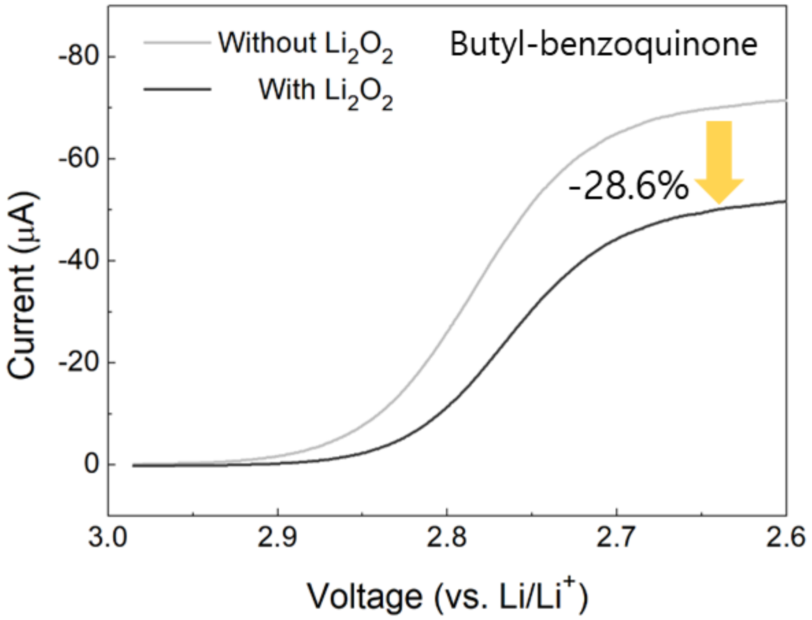

Figure S2. LSV profile with RDE using redox reaction that is unreactive toward Li_2O_2 powder. The reduction of butyl-benzoquinone, where the reduced species is inert to Li_2O_2 powder, was utilized to investigate the limiting current decrease from the decreased diffusivity with dispersed Li_2O_2 powder. The reduction in $i_{l,a}$ was observed to be reduced by approximately 28.6% because of the decreased diffusivity in the Li_2O_2-dispersed solution. This result implies that a decrease of $i_{l,a}$ of less than 28.6% indicates the regeneration of RM because of reaction with lithium peroxide.

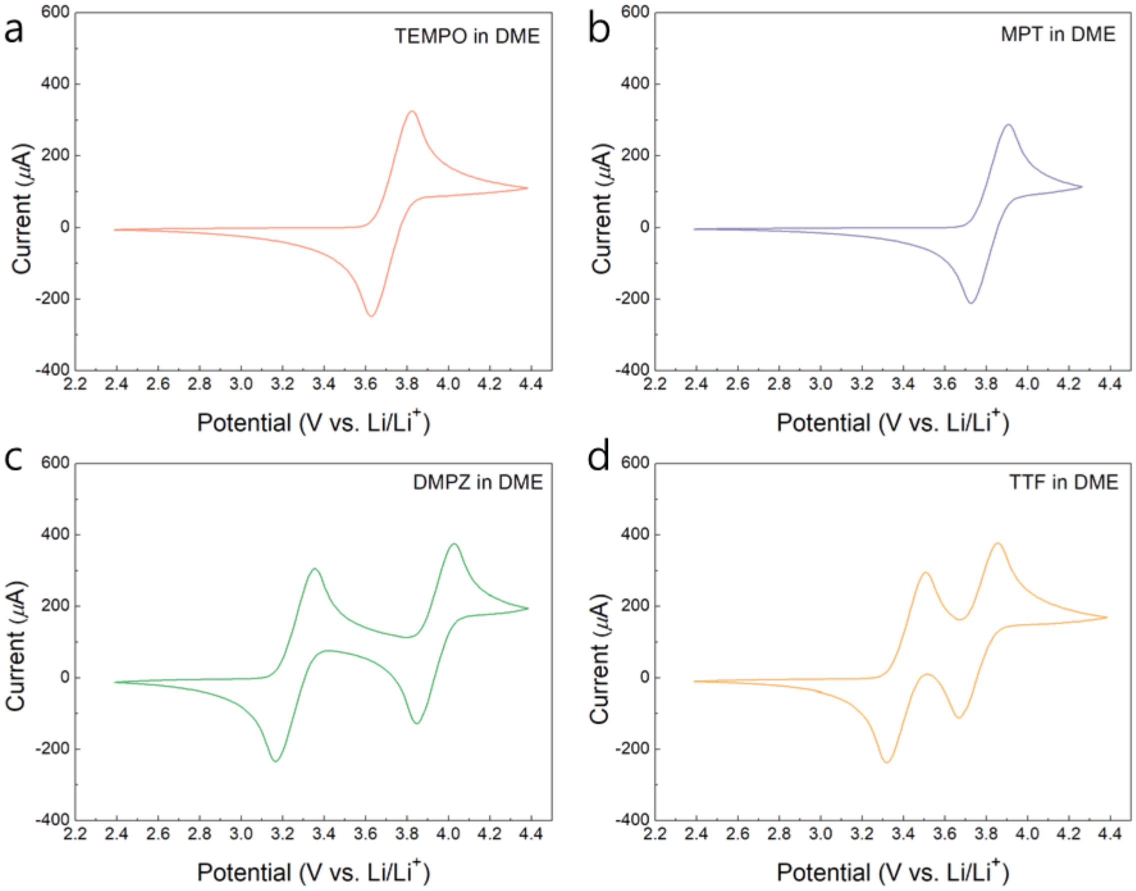

Figure S3. Cyclic voltammogram using 1 M LiTFSI in DME containing 50 mM of TEMPO (a), MPT (b), DMPZ (c), and TTF (d). The scan rate was 100 mV s^{-1}. All the redox reactions were measured to be reversible with the following calculated equilibrium redox potentials: TEMPO/TEMPO$^+$, 3.73 V; MPT/MPT$^+$, 3.82 V; DMPZ/DMPZ$^+$, 3.26 V; DMPZ$^+$/DMPZ^{2+}, 3.94 V; TTF/TTF$^+$, 3.42 V; and TTF$^+$/TTF^{2+}, 3.76 V (all the values are expressed vs. Li/Li$^+$ potential).

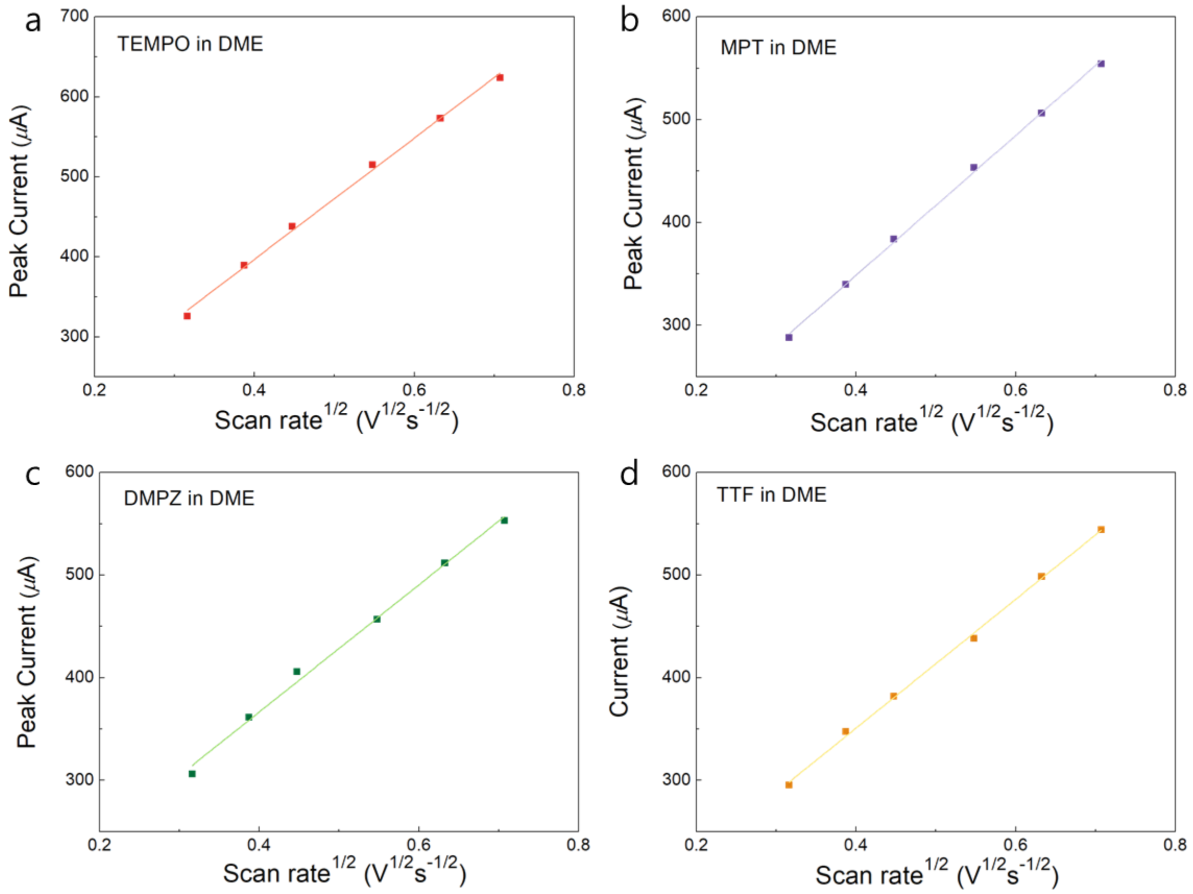

Figure S4. The plot of (scan rate)$^{1/2}$ vs. peak current of cyclic voltammogram using 1 M LiTFSI in DME containing 50 mM of TEMPO (a), MPT (b), DMPZ (c), and TTF (d) for various scan rates ranging from 100 to 500 mV^{-1}. The diffusivity of each RM was calculated from the linear relationship between (scan rate)$^{1/2}$ and the peak current using the Randles–Sevcik equation.

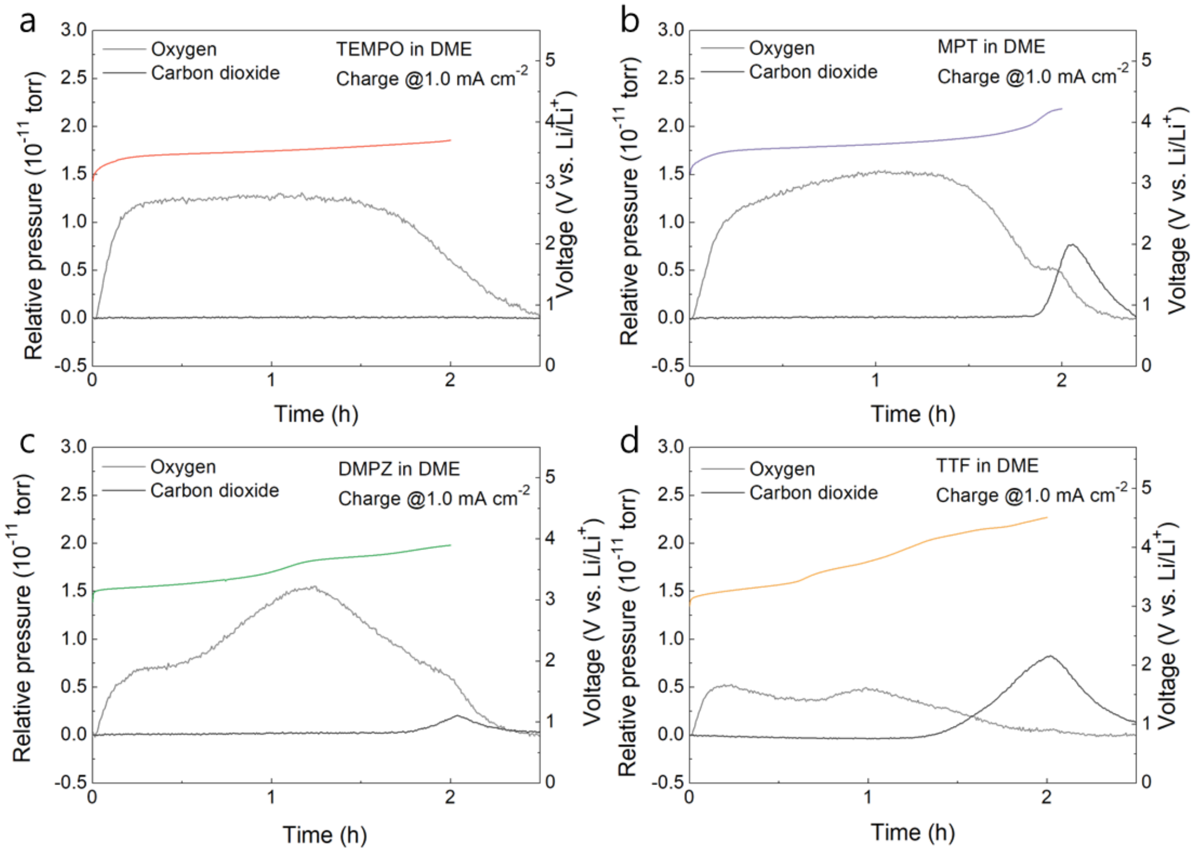

Figure S5. DEMS gas analysis while charging a lithium–oxygen battery under a current rate of 1.0 mA cm^{-2} using TEMPO (a), MPT (b), DMPZ (c), and TTF (d). The grey and black lines indicate the O_2 and CO_2 emission, respectively.

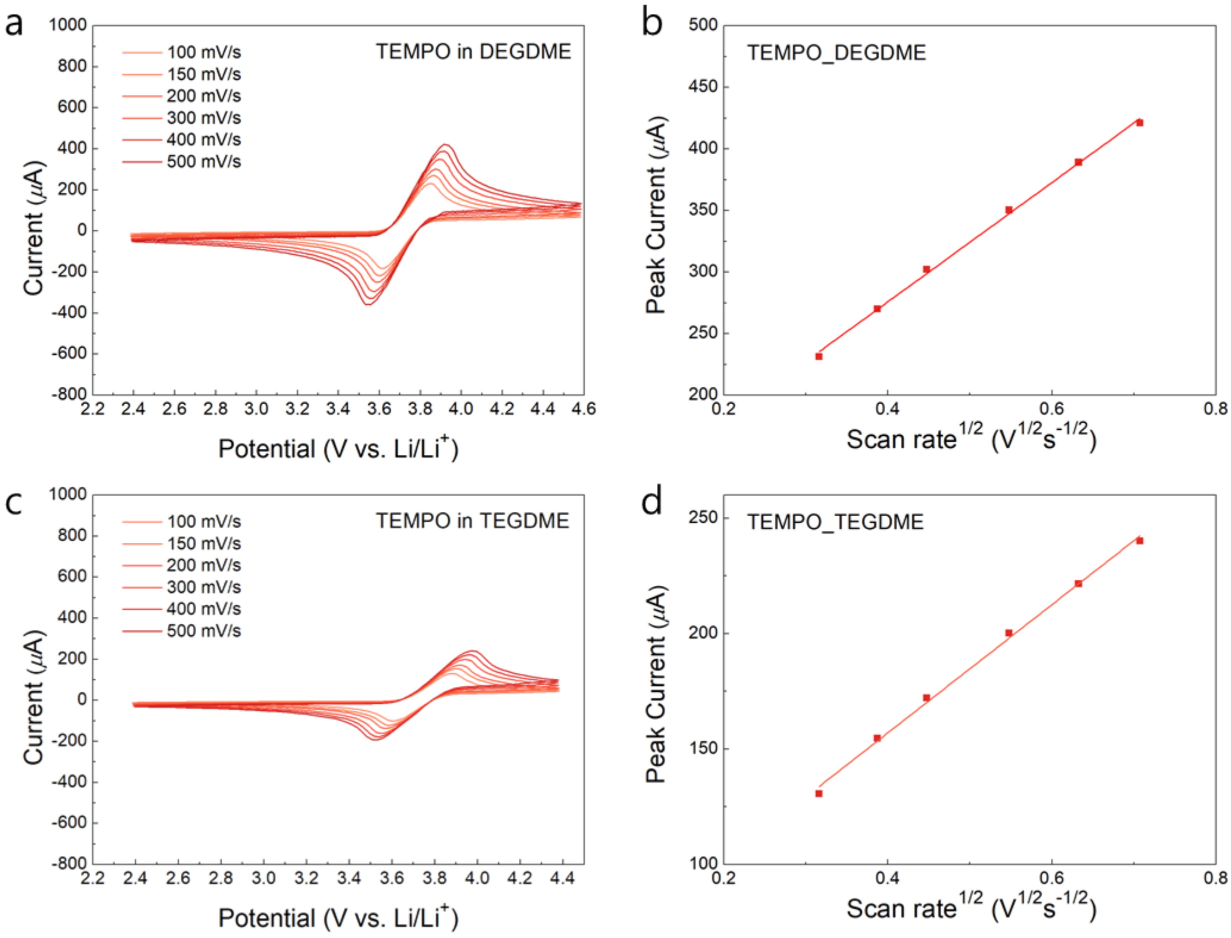

Figure S6. Cyclic voltammograms and corresponding plots of peak current vs. (scan rate)$^{1/2}$. Cyclic voltammograms of 1 M LiTFSI in DEGDME (a) and in TEGDME (c) with 50 mM TEMPO for scan rates ranging from 100 to 500 mV s^{-1}. Plots showing a linear relationship between peak current and (scan rate)$^{1/2}$ for 1 M LiTFSI in DEGDME (b) and TEGDME (d).

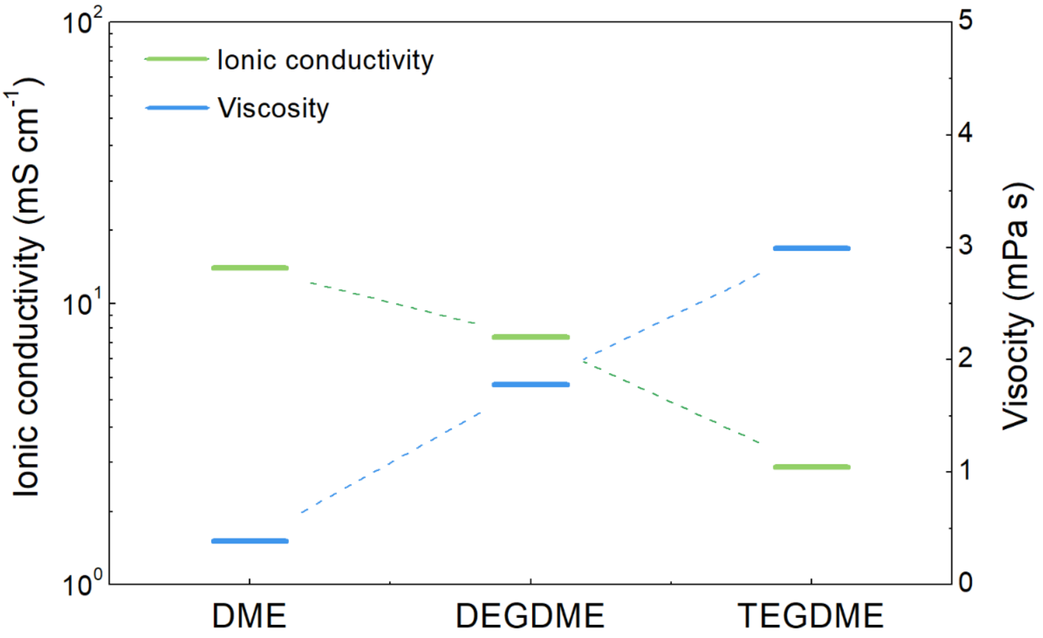

Figure S7. Ionic conductivity and viscosity of various ether-based electrolyte.[1, 2] The measured ionic conductivity is 13.39, 7.62, and 2.62 mS cm^{-1} at 300 K for 1M LiTFSI DME, 1M LiTFSI DEGDME, and 1M LiTFSI TEGDME, respectively. The electrolytes with higher viscosity have a tendency to show lower ionic conductivity. Each electrolyte exhibits slightly different electrochemical stability window,[3] and thus, the intrinsic charge cut-off stability varies as shown with the grey dotted lines in Figure 3a-d, 5b, and 5d without the use of RMs. However, with the use of RMs, the charging voltage of RMs is far below the intrinsic charge cut-off voltage of each electrolyte. Therefore, its effect is supposed to be minimal.

Reference

1. P. Zheng, X. Meng, J. Wu and Z. Liu, *Int. J. Thermophys.*, 2008, **29**, 1244-1256.
2. D. Kodama, M. Kanakubo, M. Kokubo, S. Hashimoto, H. Nanjo and M. Kato, *Fluid Phase Equilib.*, 2011, **302**, 103-108.
3. L. Carbone, M. Gobet, J. Peng, M. Devany, B. Scrosati, S. Greenbaum and J. Hassoun, *ACS Appl. Mater. Interfaces*, 2015, **7**, 13859-13865.