

Figure S1: O₂ diffusion pressure decay as a function of time and the fit to determine the D_{O2}

The fitting equation for the diffusion coefficient is obtained from the model developed by Hou et al. ¹

$$\ln\left(\frac{p(t)}{p_o}\right) = \left(\frac{k}{H_{O2}}\right) \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \left\{ \exp\left(-\frac{(2n+1)^2 \pi^2 D_{o2} t}{4L^2}\right) - 1 \right\}$$

$$k = \frac{8RTV_{liq}\rho_{liq}}{\pi^2 V_{O2} M_{w,liq}}$$

$p(t)$: Pressure drop at time t	L : Height of liquid film
p_o : Pressure at start of the experiment	V_{liq} : Volume of the liquid
H_{O2} : Henry constant for oxygen in liquid	ρ_{liq} : Density of liquid
D_{O2} : Diffusion coefficient of oxygen in liquid	$M_{w,liq}$: Molecular weight of liquid
t : Time	n= 20 (number of sums)

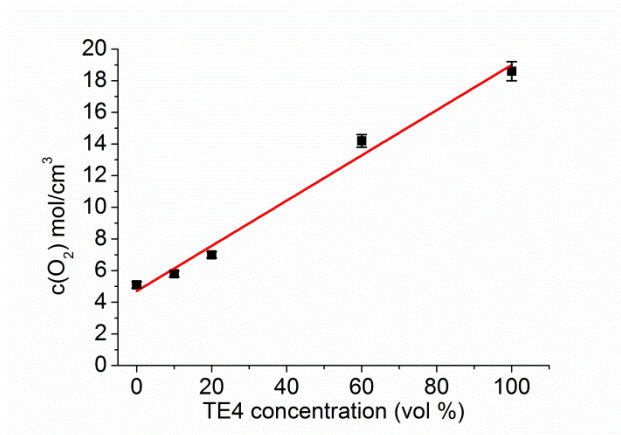


Figure S2: O₂ concentration as a function of TE4 additive percentage. Linear relation is observed between O₂ concentration increase and TE4 additive percentage

S3: Estimation of O₂ solubility for TE4 additive using method developed by Lawson et al.² and experimental data comparison

Molecular breakdown	ΔE_v^{298} (cal mol ⁻¹)	ΔV (cm ³ mol ⁻¹)
1 x CF ₃	1933	54.8
3 x CF ₂	2349	69.3
4 x CH ₂	4720	64.4
1 x CH ₃	1125	33.5
1 X -O- (ether)	8	19.0
Total	10135	241

Heat of vaporization at 25°C

$$\Delta H_v^{298} = \Delta E_v^{298} + RT = 10135 \frac{\text{cal}}{\text{mol}} + \frac{1.987 \text{ cal}}{\text{mol K}} \times 298 \text{ K} = 10727 \frac{\text{cal}}{\text{mol}}$$

Entropy of vaporization at 25°C

$$\Delta S_v^{298} = \frac{\Delta H_v^{298}}{T} = \frac{10727 \text{ cal/mol}}{298 \text{ K}} = 36 \frac{\text{cal}}{\text{mol K}}$$

Molar volume of O₂ for open chain compound

$$V_{O_2} = -19.85 + 15.90 \ln \Delta S_v^{298} = 37.12 \frac{\text{cm}^3}{\text{mol}}$$

Mol fraction of O₂

$$\ln x_{O_2} = \ln x_{O_2}^i - \frac{\bar{V}_{O_2}(\delta - \delta_{O_2})^2}{RT} - \left[\ln(\bar{V}_{O_2}/V) + \left(1 - \frac{\bar{V}_{O_2}}{V}\right) \right]$$

With $x_{O_2}^i = 17.638 \times 10^{-4}$ and $\delta_{O_2} = 5.7 \text{ cal/cm}^3$

$$\ln x_{O_2} = \ln 17.638e^{-4} - \frac{37.12(6.48 - 5.7)^2}{592} - \left[\ln(37.12/241) + \left(1 - \frac{37.12}{241}\right) \right]$$

$$\ln x_{O_2} = -5.354$$

$$x_{O_2} = 4.7 \times 10^{-3}$$

Estimated $\text{cm}^3 \text{O}_2 / 100 \text{ mL liquid}$

$$\frac{\text{cm}^3 \text{O}_2}{100 \text{ mL liquid}} = \frac{100 \times x_{O_2} \times 24465}{V} = 47.71$$

Experimental result $\text{cm}^3 \text{O}_2 / 100 \text{ mL liquid}$

$$\begin{aligned} \frac{\text{cm}^3 \text{O}_2}{100 \text{ mL liquid}} &= TE4 H_{O_2} \times 1 \text{ bar} \times \text{molar Volume } O_2 @ 25C, 1 \text{ bar} \times 100 \text{ mL} = 18.6 \text{ mol m}^{-3} \\ &\times 24.43 \frac{\text{L}}{\text{mol}} = 45.43 \pm 0.15 \end{aligned}$$

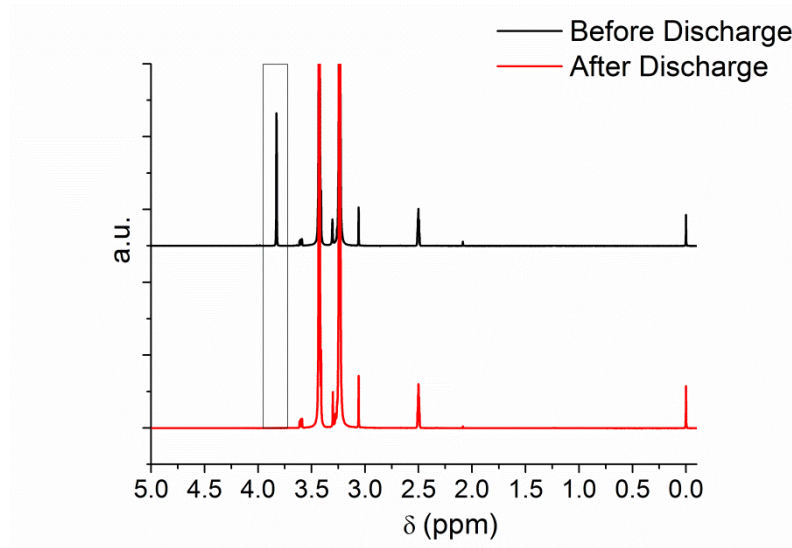


Figure S4: ^1H NMR of 0.1 M LiClO_4 :DME+20 vol% 1-methoxyheptafluoropropane (alpha fluorinated additive) before discharge and after discharge at 100 mA g^{-1} up to 2V

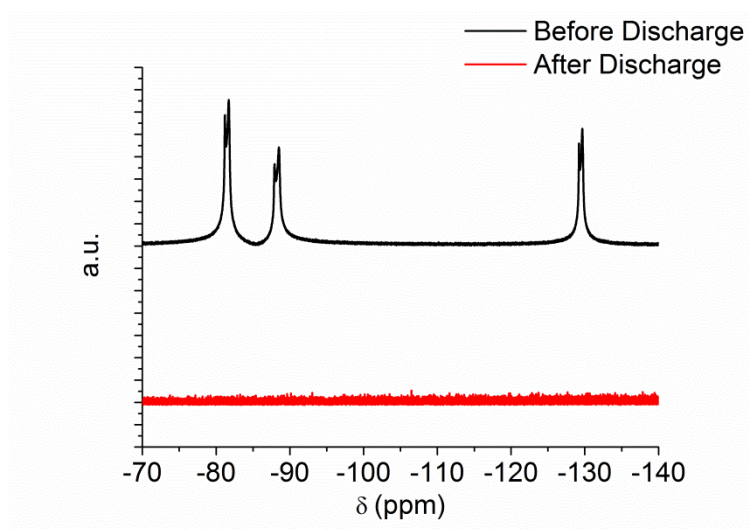


Figure S5: ^{19}F NMR of 0.1 M LiClO_4 :DME+20 vol% 1-methoxyheptafluoropropane (alpha fluorinated additive) before discharge and after discharge at 100 mA g^{-1} up to 2V

S6 The assignment of the signal for the ^1H NMR and ^{19}F NMR of TE4 additive:

The assignment for the ^1H NMR peak of TE4 additive is as follow (400MHz, CDCl_3 , RT) $\delta = 3.87\text{-}3.79$ ($\text{CH}_2\text{-O}$, m, 2H), $3.51\text{-}3.44$ (O-CH_2 , m, 2H) $2.48\text{-}2.32$ ($\text{CH}_2\text{-CF}_2$, m, 2H) , 1.60 ($\text{CH}_2\text{-CH}_3$,m, 2H) 0.92 (CH_3 , t, 3H). The assignment for the ^{19}F NMR peak of TE4 additive is as follow: (300MHz, DMSO-d_6 , RT) $\delta = -78.93$ ($\text{CF}_3\text{-S}$, s ,6F), -80.94 (CF_3 , s, 3F), -112.99 ($\text{CF}_2\text{-CH}_2$, s, 2F), -124.31 (CF_2 , s, 2F), -129.19 ($\text{CF}_2\text{-CF}_3$, s, 2F).

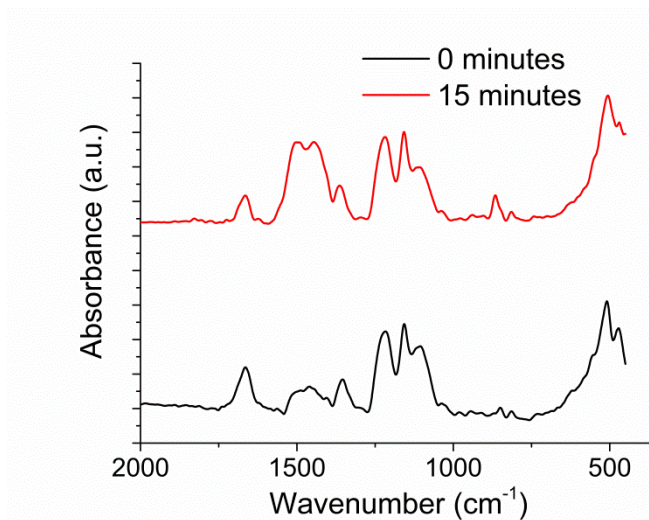


Figure S7: FTIR spectra of cathode discharged using 0.1 M LiTFSI:TEGDME+20 vol % TE4 electrolyte. The measurements were taken at 0 minutes and after 15 minutes of exposure to the air

References

- 1 H. Ying and R. E. Baltus, *Ind. Eng. Chem. Res.*, 2007, **46**, 8166.
- 2 D. D. Lawson, J. Moacanin, K. V. Scherer, T. F. Terranova and J. D. Ingham, *J. Fluor. Chem.*, 1978, **12**, 221.