Supporting information to:

Unravelling kinetics and mass transport effects on two-electron storage in radical polymers battery

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Electrode preparation

P(GTENMPO-co-GPy) and P(GTENMPO-co-GPy) gel were synthesized as previously reported. The working electrodes were prepared by mixing a specific amount of radical polymer, Super P carbon, together with poly(vinylidene fluoride) (PVdF) (mass ratio: 3/6/1) in NMP to form a slurry. Then the slurry was coated on an aluminum foil current collector via doctor blade method with a thickness of ~100 µm. The electrodes were dried in vacuo at 60 °C for 12 h to remove the solvent and cropped into cycles with a diameter of 10mm. The average areal loading of active polymer was calculated 0.3 mg.cm⁻² with standard deviation 0.07 mg.cm⁻². The cropped electrode was stored in the glove box for cell assembling directly.

Electrochemistry characterization

The electrochemical performance of polymer/SP composites was measured with 2032 coin cells assembled in an Argon-filled glovebox. Lithium foil was used as the counter and reference electrode, and porous glass fibre (What-man) was used as a separator. The electrolyte was LiClO₄ (1 mol/L) in dimethyl carbonate/ethylene carbonate (DMC/EC 1/1, v/v), and a 40 μ L of electrolyte was added for each cell. Cyclic voltammetry of both PGTEMPO and GTEMPO gel was performed on CHI 760D electrochemical working station with scan rate 0.2 mV/s in three different potential windows 2.0-3.2 V, 3.0-4.0V and 2.0-4.0V, respectively, and three cycles were tested. Galvanostatic cycling tests of the assembled cells of both GTEMPO and GTEMPO gel were performed on a LAND CT2001A system in two potential windows 3.0–4.0V and 2.0-4.0V. For cycling test, the charge/discharge rate was set as 1C (111mA.g⁻¹), for C-rate test, 1C, 2C, 5C, 10C and 30C was adopted with 1C equal to 111mA.g⁻¹. Electrochemical impedance spectroscopy (EIS) were recorded on a ZIVE mp2 multichannel electrochemical workstation with potential amplitude set at 10mV and frequencies ranged from 0.01–2500 Hz. For PGTEMPO, PGTEMPO gels and PTMA cells, electrochemical impedance spectra (EIS) at different open-circuit voltage were obtained. Briefly, the cell was charged or discharged on the LAND CT2001A system to a specific potential point; then, the cell was disconnected and using the Zive mp2 system to measure the EIS at the open circuit potential point. The equivalent circuit for all the composites was obtained by fitting the spectra using ZIVE Lab ZMAN[™] 2.4 software.

Table S1. Data of	polymers used	in this v	vork
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Entry	Mn (<i>Ð</i>)° kDa	TEMPO density (mmol/g) ^d	Theoretical capacity (1e) (mAh g ^{-1)e}	Theoretical capacity (2e) (mAh g ⁻¹) ^e
P(GTEMPO-co-GPy) ^a	10.6 (2.37)	3.17	84	168
P(GTEMPO-co-GPy) Gel ^a	-	2.92	78	156
PTMA ₄₈₃ b	90.3 (1.24)	3.09	84	168

^{a, b} Polymers were from our previous publications Polym. Chem., 2017,8, 1815-1823 and Polym. Chem., 2020,11, 4155-4163, respectively; ^c M_n was determined by SEC with linear polystyrene as standards; ^d TEMPO density was determined by electron spin resonance; ^e Theoretical capacity (C) was calculated according to C (mAh g⁻¹)=96485*n/3.6/MW, where MW is the molecular weight per radical (g/mol) and *n* is the number of electron transfer.

Computational Methodology

All *ab initio* and density functional theory (DFT) calculations were performed in ORCA 4.2.1.¹ The B3LYP functional was used in conjunction with the Becke-Johnson damped D3 dispersion correction² (D3BJ) to optimize geometries and obtain harmonic frequencies. For all species in this study, were verified our conformations were true minima possessing no imaginary frequencies. Improved single-point energies were then calculated with DLPNO-CCSD(T). For B3LYP calculations, the def2-TZVP basis set was used,³ in conjunction with the RIJCOSX approximation and a def2/J auxiliary basis set.⁴ To minimize potential numerical artefacts, 'Grid7' and 'GridX7' was used in conjunction with the 'NoFinalGrid' keyword. We turned off the pre-screening for frequency calculations to avoid reported issues with RI-integral prescreening for analytical hessian calculations. For DLPNO-CCSD(T) calculations,⁵ the aug-cc-pVTZ basis set was used,⁶⁻⁷ in conjunction with the RIJCOSX approximation cc-pVTZ/C auxiliary basis set and the 'AutoAux' keyword.^{8, 4} In addition, 'TightPNO' cut-offs were applied. 'VeryTight' SCF convergence criteria was used for all improved energy calculations.



Figure S1. Swelling properties of P(GTENMPO-co-GPy) gel in different electrolyte solvents solubilized with 1 M of LiPF₆.



Figure S2. SEM morphologies of (A and B) the electrode composite of PGTEMPO/SPC/PVDF at 3/6/1; (C and D) PGTEMPO Gel/SPC/PVDF at 3/6/1.



Figure S3. (A) Initial charge/discharge profile and (B) 2^{nd} and 100^{th} cycle of the electrode composed of polymer/SP carbon/PVDF of 3/6/1 and the charge/discharge current density was at 0.11 A g⁻¹.



Figure S4. Galvanostatic charge/discharge profile of SPC/PVDF (9/1) electrode at 1C in a potential window of 2-4 V; current density 0.11 A g⁻¹. Inset: CV curve at 0.2 mV s⁻¹.



Figure S5. CV curves of PTMA₄₈₃/SPC/PVDF (3/6/1) electrode at different scan rates in a potential window of 2-4 V.



Figure S6. Differential scanning calorimetry (DSC) curves of PTMA₄₈₃ and P(GTEMPO-co-GPy) gel (second run) were obtained on PerkinElmer DSC. The temperature was ramped up at a rate of 10 °C min⁻¹.

Charge-transfer kinetics analysis

To obtain the apparent diffusion coefficient of electron transfer, D_{app} , the peak current I_p was plotted against the square root of scan rate, $v^{1/2}$, and D_{app} can be obtained through the Randles-Svecick equation:

$$i_p = 268600n^{3/2}AD^{1/2}C_0^*\nu^{1/2}$$
 Eq 1

It is noted that the surface area of gel particles is calculated by assuming that gel particles were close to spheres and had good contact with added carbon additives since a gel/carbon/binder ratio of 3/6/1 was used (Figure S2). As such, the total surface area A_{total} can be estimated as follows:

$$A_{total} = \frac{6m_{gel}}{\rho d}$$
 Eq 2

where the particle diameter *d* was approximately 10 μ m obtained from optical microscopy; the gel density ρ is approximately 1.0 g cm⁻³; m_{gel} is the mass loading of gel per electrode; The radical concentration C₀^{*} of gel particles was 2.6 M after considering the swelling ratio of 1.5 in the tested electrolyte DMC/EC at 1/1 (v/v) (Supporting Information).

Generally, D_{app} is a combining effect of electron transfer D_{et} and physical diffusion of polymer segments D_{phys} which is expressed by:

$$D_{app} = D_{et} + D_{phys}$$
 Eq 3

Previous work by Murray demonstrated that when the concentration of redox sites was above 1 M, the contribution from D_{phys} could be negligible. Thus, the concentration dependent D_{et} is directly reflected by D_{app} . The homogeneous electron self-exchange rate constant k_{ex} can be calculated from Dhams-Ruff equation 4:

$$D_{app} = \frac{1}{6} C_0^* \delta^2 k_{ex}$$
 Eq 4

To estimate the heterogeneous electron transfer rate constants k_0 for both redox reaction couples, we adopt a few different approaches. The first one is the Nicholson method as Eq 5:

$$k_0 = \psi \left(\pi D_{app} \frac{nF\nu}{RT} \right)^{1/2}$$
 Eq 5

where the ψ is determined by fitting the overpotentials η obtained at different scan rates to the η - Ψ curve established by assuming semi-infinite diffusion, α =0.5, the same diffusion coefficient for the reversible electron transfer process. The resulting Ψ was plotted against the reciprocal of the square root of the scan

rate $v^{-1/2}$. k_0 for redox couple (I) and (II) were calculated from the slop as k_0^{1} of 3.96x10⁻⁶ and k_0^{11} of 3.87x10⁻⁷ cm s⁻¹, respectively.



Figure S7. ψ - ΔE_p plot derived by Nicholson. (•) were corresponding to the redox couple (I) (NO⁺/NO[•]) and (•) were corresponding to the redox couple (II) (NO[•]/NO⁻).

Ion diffusion analysis

The lithium-ion diffusion coefficient D_{ion} at different charge/discharge state V_{c-d} were calculated according to the following equation:

$$D_{ion} = \frac{R^2 T^2}{2n^4 F^4 C^2 \sigma^2}$$
 Eq 6

where the Warburg coefficient σ is given by the relationship of $Z' = \sigma \omega^{-1/2}$. When Z' was plotted against the reciprocal of the square root of frequency, $\omega^{-1/2}$ in the low-frequency region, such as <1 Hz. The calculated ion diffusion coefficient D_{ion} at those four potentials were listed in Tale 1.

The first one is the Nicholson method as Eq 7:

$$k_0 = \psi \left(\pi D_{app} \frac{nF\nu}{RT} \right)^{1/2}$$
 Eq 7

where the overpotentials, η , derived from CV at different scan rates were fitted to the η - Ψ curve established by Nicholson assuming semi-infinite diffusion, α =0.5, the same diffusion coefficient for the reversible electron transfer process. The resulting Ψ was plotted against the reciprocal of the square root of the scan rate v^{-1/2}.



Figure S8. Ion diffusion analysis of PTMA₄₈₃/SPC/PVDF (3/6/1) electrode at different charge/discharge states, V_{c-d} . (A) galvanostatic charge/discharge profile with indicated V_{c-d} for the electrochemical impedance spectra (EIS) measurement, (B) EIS at different V_{c-d} , and (C) Z'- $\omega^{-1/2}$ plot for the calculation of ion diffusion coefficient.

Radical polymers	V _{c-d} (V vs. Li⁺/Li)	R _s (Ω)	R _{ct} (Ω)	D _{ion} (cm ² s ⁻¹)	logDion
	Charge 2.5	6	547	6.14x10 ⁻¹³	-12.21
	Charge 3.0	18	487	2.22x10 ⁻¹²	-11.65
	Charge 3.5	3.6	479	3.26x10 ⁻⁹	-8.49
P(GTEMPO-co-GPy) Gel	Discharge 3.5	3.6	358	1.24x10 ⁻⁸	-7.91
	Discharge 2.5	2.3	487	2.97x10 ⁻¹²	-11.53
	Charge 3.0	26.8	987	3.69x10 ⁻¹³	-12.43
	Charge 3.4	27.6	784	2.48x10 ⁻¹³	-12.61
	Charge 3.6	30.2	804	2.11x10 ⁻⁹	-8.68
	Discharge 2.3	29.0	728	3.46x10 ⁻¹³	-12.46
PTMA ₄₈₃	Discharge 2.6	27.8	783	2.72x10 ⁻¹³	-12.57
	Discharge 3.6	31.3	747	5.02x10 ⁻¹⁰	-9.30

Table S2. Electrode kinetics parameters obtained from EIS for P(GTEMPO-co-GPy) Gel and PTMA₄₈₃ at different charge/discharge states, V_{c-d} .

Ab initio calculation. To verify the reaction rates obtained by the experimental electrochemistry, we apply a theoretical calculation to obtain the kinetics for both redox couples. Marcus-Hush formalism has been successfully used to calculate k_0 and k_{ex} for the redox couple (I) of small nitroxide radicals. However, it is inapplicable for a redox polymer system as evidenced by Oyaizu and Nishide,⁹ who have developed a revised model by including the physical diffusion of polymer chain segments.

$$k_0 = \kappa_{el} \frac{3D_{phys}}{2L} exp\left(-\frac{\lambda}{4k_bT}\right)$$
 Eq 8

In our case, λ is the reorganization energy, defined as the energy required to reorganize the radial or its redox product before the electron transfer occurring. This reorganization energy is composed of inner sphere (λ_i) and outer sphere (λ_o) components. The former is defined as the energy associated with geometry changes to distort radicals into their products without an electron transfer occurring, and the latter depending on the solvent relation around the redox reaction species. Although this revised model has successfully predicted the k_{ex} and k_0 for various redox-active polymers, it has not been used to calculate the reaction rates of the reduction couple for nitroxide radicals. We have managed to obtain the λ_o according to Eq. 9 for the heterogeneous reaction in a radical gel cell.

$$\lambda_o = \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{\delta} \right) \left(\frac{1}{n_s^2} - \frac{1}{\varepsilon_s} \right)$$
 Eq 9

For a TEMPO radical, $a_1=a_2=0.31$ nm and $\delta=0.8$ nm, $n_s=1.39$ and $\varepsilon_s=31$ were calculated based on a mixture of 1 M LiClO₄ in DMC/EC (1/1. v/v) in this work. The calculated λ_0 was 0.686 eV. While the λ_i is determined by the geometric reorganization of nitroxide radicals, with oxoammonium cations and aminoxyl anions preferring different molecular configurations. Using TEMPO as a truncated model for the reacting sites of polymer gels, notable geometric parameters that are sensitive to the redox states are listed in **Table 1**. Taking the N-O bond length as an example, we note that the equilibrium distance decreases by 0.091 Å upon oxidation of TEMPO but increases by 0.135 Å upon its reduction. Similarly, bond angles associated with the N-atom undergo larger absolute changes upon radical reduction than radical oxidation. From a theoretical point of view, nitroxides have a significant level of radical character on the N atom that results from mixing the formally doubly occupied N 2p orbital with the formally singly occupied O 2p orbital. This mixing gives the N-O bond of nitroxide radicals some double-bond character and decreases the N-pyramidalisation angle while also increasing the CNO and CNC bond angles. However, some parameters, such as the C-N bond lengths, have more changed upon TEMPO radicals' oxidation than upon reduction (although these changes are smaller than those observed in the N-O bond length). Overall λ_i for the redox couple (I) and (II) are 0.468 and 0.676 eV, respectively, as indicated with bond length and angles in Figure 5. The larger energetic change associated with the reduction couple compared to the oxidation one suggests the geometry of the nitroxide radical more closely resembles the oxoammonium cation rather than the aminoxyl anion.

Oxidation State	N-O bond length (Å)	C-N bond length (Å)	CNO bond angle (°)	CNC bond angle (°)	N-Pyramidalisation angle (°)
TEMPO⁺	1.184	1.530	118.0	124.0	0.3
TEMPO	1.275	1.492	115.9	123.9	6.8
TEMPO-	1.410	1.481	109.9	117.2	16.4

Table S3. Key equilibrium geometric parameters for the three oxidation states of TEMPO.



Figure S9. Electrochemical performance of P(GTENMPO-co-GPy) gel electrode. Galvanostatic charge/discharge profile at different C-rate with a potential window of (A) 3-4 V and (B) 2-4 V, (C) discharge capacities at different C-rate and (D) Ragone plot for 1e⁻ (•) and 2e⁻ (•) storage

Raw Energies

Table S4. Raw DLPNO-CCSD(T)/aug-cc-pVTZ electronic energies for the different oxidation states of TEMPO calculated on geometries optimized with B3LYP-D3BJ/def2-TZVP.

Optimized Geometry	Oxidation State	Electronic Energy (Hartree)
TEMPO•	Radical	-482.914238
TEMPO•	Cation	-482.648129
TEMPO•	Anion	-482.901010
TEMPO ⁺	Cation	-482.664586
TEMPO ⁺	Radical	-482.894960
TEMPO ⁻	Anion	-482.930061
TEMPO ⁻	Radical	-482.893618

Gas-phase Geometries

TEMPO•

02

С	0.02756963928902	-0.03577469440479	-1.32219908256559
С	0.46109693102079	1.43376029059928	-1.23943180740089
С	-0.05506623919649	2.15067276510561	0.00000055514885
С	0.46109912991921	1.43375974913967	1.23943164407115
С	0.02756992692285	-0.03577471285119	1.32219890523539
N	0.22720758806525	-0.70920825764151	-0.0000006364085
С	0.90145451454210	-0.76711344323531	-2.34300260791036
С	-1.44813159732193	-0.16229604502149	-1.73256709225958
н	0.12911735697998	1.93407024089280	-2.15201314685085
н	1.55469562581204	1.47586799997033	-1.23668095715441
н	-1.14716002797551	2.18875559107620	0.00000169793380
н	0.28844803954393	3.18760476620103	0.00000045852387
н	0.12912171037495	1.93406999197987	2.15201354479649
н	1.55469778993104	1.47586609048480	1.23667861424766
с	-1.44813163402834	-0.16229435991001	1.73256670787408

С	0.90145331647601	-0.76711437454212	2.34300296799743
0	0.12197908735547	-1.98120705332167	-0.00000013646207
н	1.94639395168760	-0.75527272523117	-2.03008036992237
н	0.82238382971963	-0.26651801135016	-3.30963028702653
н	0.58807042480042	-1.80255944875258	-2.45270840591037
н	-2.10356586384019	0.44077176503265	-1.10580426068598
н	-1.76075115819994	-1.20335549567012	-1.65909880893588
н	-1.57249443429402	0.16719549652302	-2.76563133092800
н	-2.10356534167413	0.44077307815925	1.10580301975632
н	-1.57249445468183	0.16719825375558	2.76563059493835
н	-1.76075166478967	-1.20335368664814	1.65909936535221
н	1.94639292124801	-0.75527516180157	2.03008117782489
н	0.58806767111770	-1.80255991391136	2.45270859450610
Н	0.82238296119604	-0.26651869462688	3.30963050944713

TEMPO+

11

С	0.03504140521526	-0.03143610356693	-1.35366658229718
С	0.47216853641554	1.44085884404590	-1.24631719194191
С	-0.03116517207391	2.15263955035412	0.00000101400949
С	0.47217197491611	1.44085714928225	1.24631675345013
С	0.03504145851505	-0.03143681167641	1.35366660423857
N	0.28128521468720	-0.70859797114117	-0.0000010020036
С	0.84540469549382	-0.78464046781562	-2.40024744022115
С	-1.47355241024781	-0.17722585726153	-1.64649099381431
Н	0.11816280552059	1.93181836236458	-2.15391941396425
н	1.56419043420499	1.47965857675892	-1.27409700943070

Н	-1.11978501721655	2.22681132922397	0.00000268101395
Н	0.34064078431941	3.17792171937123	0.00000108681050
Н	0.11817077249056	1.93181677514305	2.15392070954539
Н	1.56419406747676	1.47965411597091	1.27409251721608
С	-1.47355249667805	-0.17722393041821	1.64649047073985
С	0.84540272555519	-0.78464297405101	2.40024787559493
0	0.67774682656020	-1.82316040223810	-0.00000045056711
Н	1.90240488520064	-0.82488475872702	-2.13689688710874
Н	0.74917943541382	-0.23949840403306	-3.33863224863460
Н	0.48226552835909	-1.79822897045738	-2.55547533121891
Н	-2.09253199887808	0.46679636828820	-1.03112821563211
Н	-1.80050618906784	-1.21062186232919	-1.53634287148139
Н	-1.61304615040424	0.11168748621044	-2.68793280617792
Н	-2.09253203762422	0.46679146082009	1.03112062734755
Н	-1.61304779190497	0.11169957346530	2.68792925317629
Н	-1.80050485463552	-1.21062131789941	1.53635180848610
Н	1.90240306520276	-0.82488922694496	2.13689820985465
Н	0.48226168981853	-1.79823091410091	2.55547497625497
н	0.74917781336568	-0.23950133863804	3.33863295495219

TEMPO⁻

-11

С	0.06027903992262	-0.02941123044347	-1.26587668222299
С	0.48185979142886	1.44807566353251	-1.24237644498884
С	-0.00839848402363	2.18168883184709	-0.00000010397763
С	0.48185918306506	1.44807539397160	1.24237646973387
с	0.06027876930215	-0.02941174918156	1.26587643838459

Ν	0.45968723136488	-0.69108804746394	-0.00000015412737
С	0.85454181409704	-0.74696437526496	-2.36648035049931
С	-1.44186826387632	-0.18260857443778	-1.59557651949504
Н	0.12492504296476	1.93915097137338	-2.15531400156949
н	1.57696839778072	1.48890582059884	-1.26025192556392
н	-1.10112400619677	2.23585081113570	-0.00000037940765
н	0.35164425793661	3.21767500596271	0.0000005466292
н	0.12492356662488	1.93915086181314	2.15531356225054
Н	1.57696770210646	1.48890565290620	1.26025305891456
С	-1.44186834337393	-0.18261000567285	1.59557647254132
С	0.85454202717800	-0.74696404729131	2.36648029880447
0	0.02313494184570	-2.02641160911465	-0.00000026554277
Н	1.92319145326072	-0.67542847470438	-2.14961951148610
н	0.65387883171140	-0.30475127513425	-3.34908971501091
н	0.57803083651290	-1.80022466954036	-2.36129772542594
н	-2.06480616892473	0.54437061378326	-1.07284367081061
н	-1.71805820922559	-1.19102338181276	-1.27742575379902
н	-1.62786851572906	-0.07186055148390	-2.66889424272118
н	-2.06480702707460	0.54436836936748	1.07284332068736
н	-1.62786879127358	-0.07186193144408	2.66889415311306
н	-1.71805746582966	-1.19102513032081	1.27742595775148
н	1.92319153537723	-0.67543087370890	2.14961762927217
н	0.57802939237460	-1.80022389691047	2.36130105997368
н	0.65388146067329	-0.30474817236148	3.34908897055876

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