Mediating anion-cation interactions to improve aqueous flow battery electrolytes

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Supporting Information

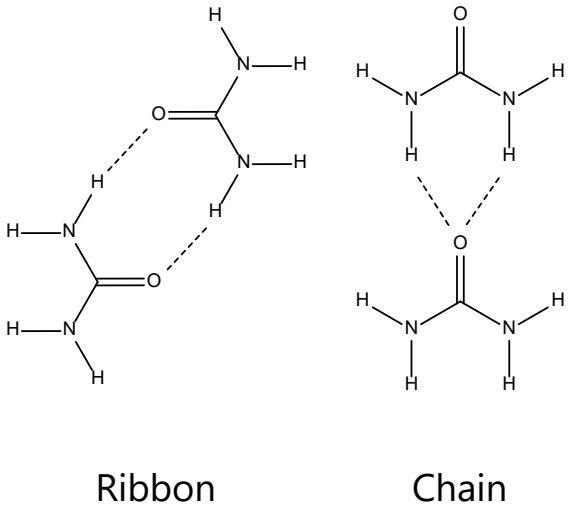

Fig. S1: Structure of a urea ribbon and a chain dimer, based on reference [1].

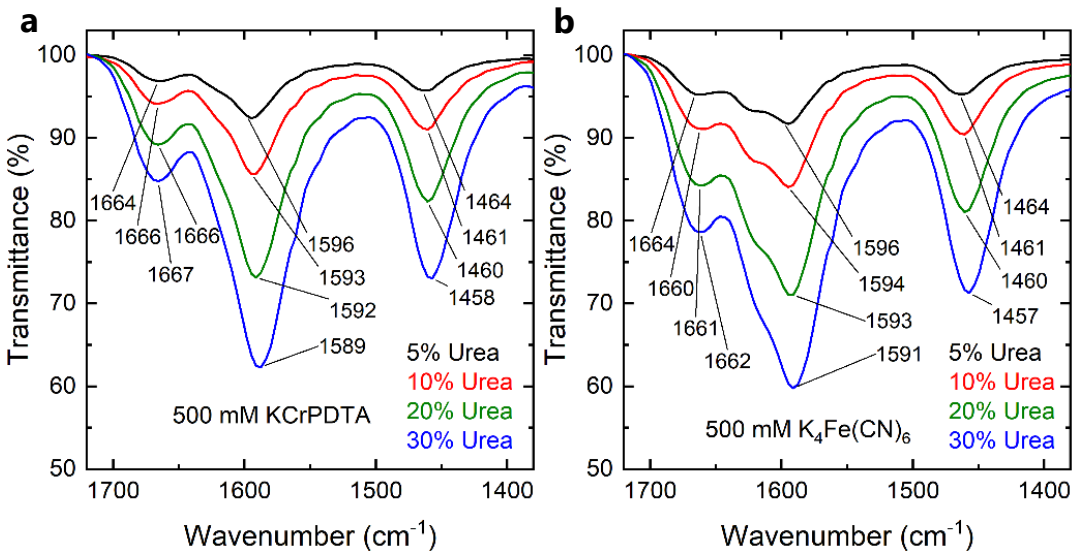

Fig. S2: IR spectra of urea solutions with **a,** 500 mM KCrPDTA or **b,** $K_4Fe(CN)_6$. The spectra of 500 mM respective salt in pure water were subtracted to obtain the urea signatures.

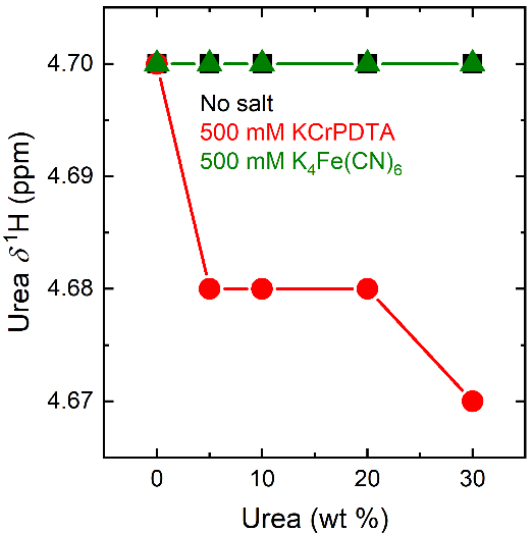

Fig. S3: NMR chemical shifts δ^1H of water in water, 500 mM KCrPDTA, or $K_4Fe(CN)_6$ solutions, respectively.

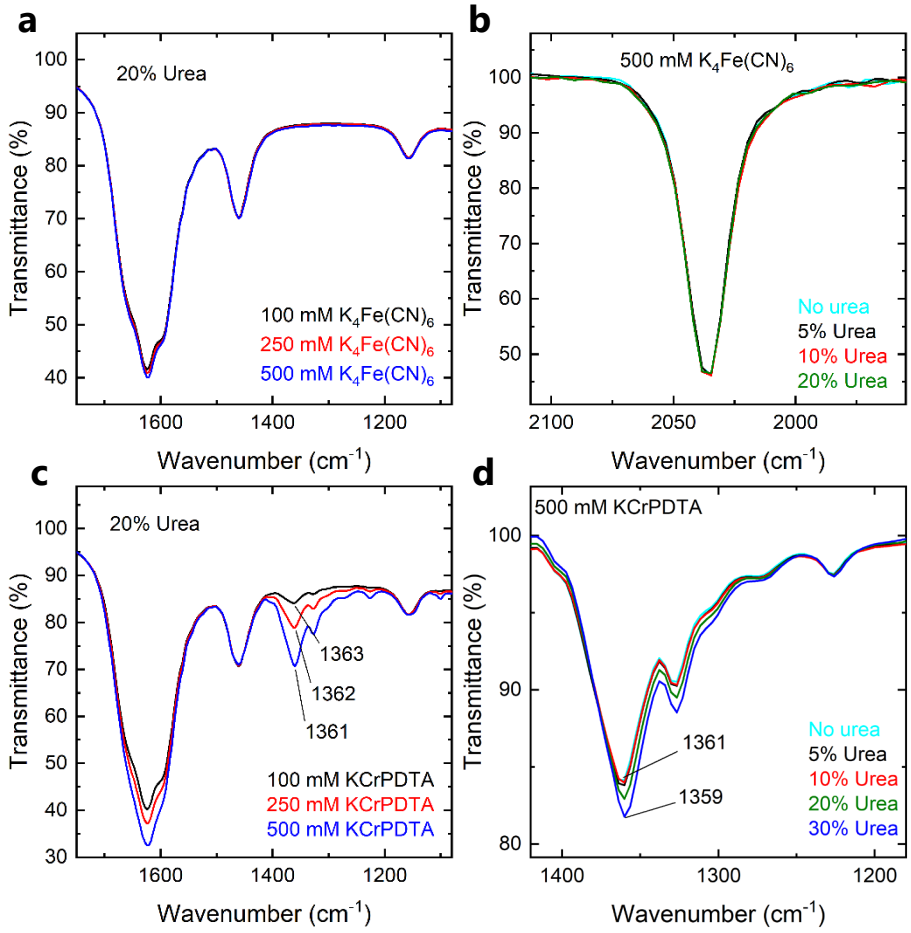

Fig. S4: Raw IR spectra of **a,** 100 mM, 250 mM and 500 mM $K_4Fe(CN)_6$ solutions with 20% urea, **b,** 500 mM $K_4Fe(CN)_6$ at different urea concentrations, **c,** 100 mM, 250 mM and 500 mM KCrPDTA solutions with 20% urea, and **d,** 500 mM KCrPDTA at different urea concentrations. For samples in a and c no references were subtracted.

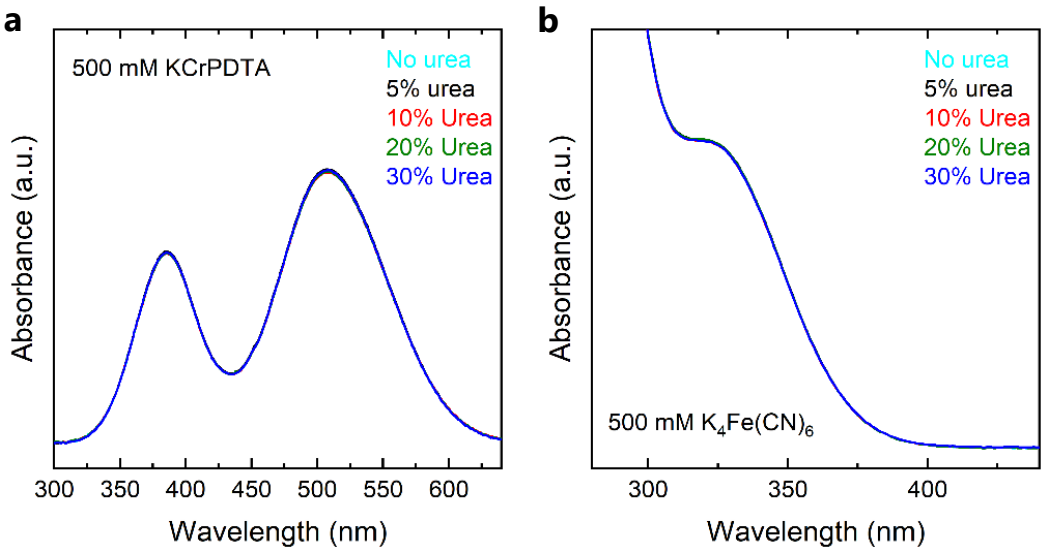

Fig. S5: UV-vis spectra of urea solutions with **a,** 500 mM KCrPDTA (diluted 250x) or **b,** 500 mM $K_4Fe(CN)_6$ (diluted 500x).

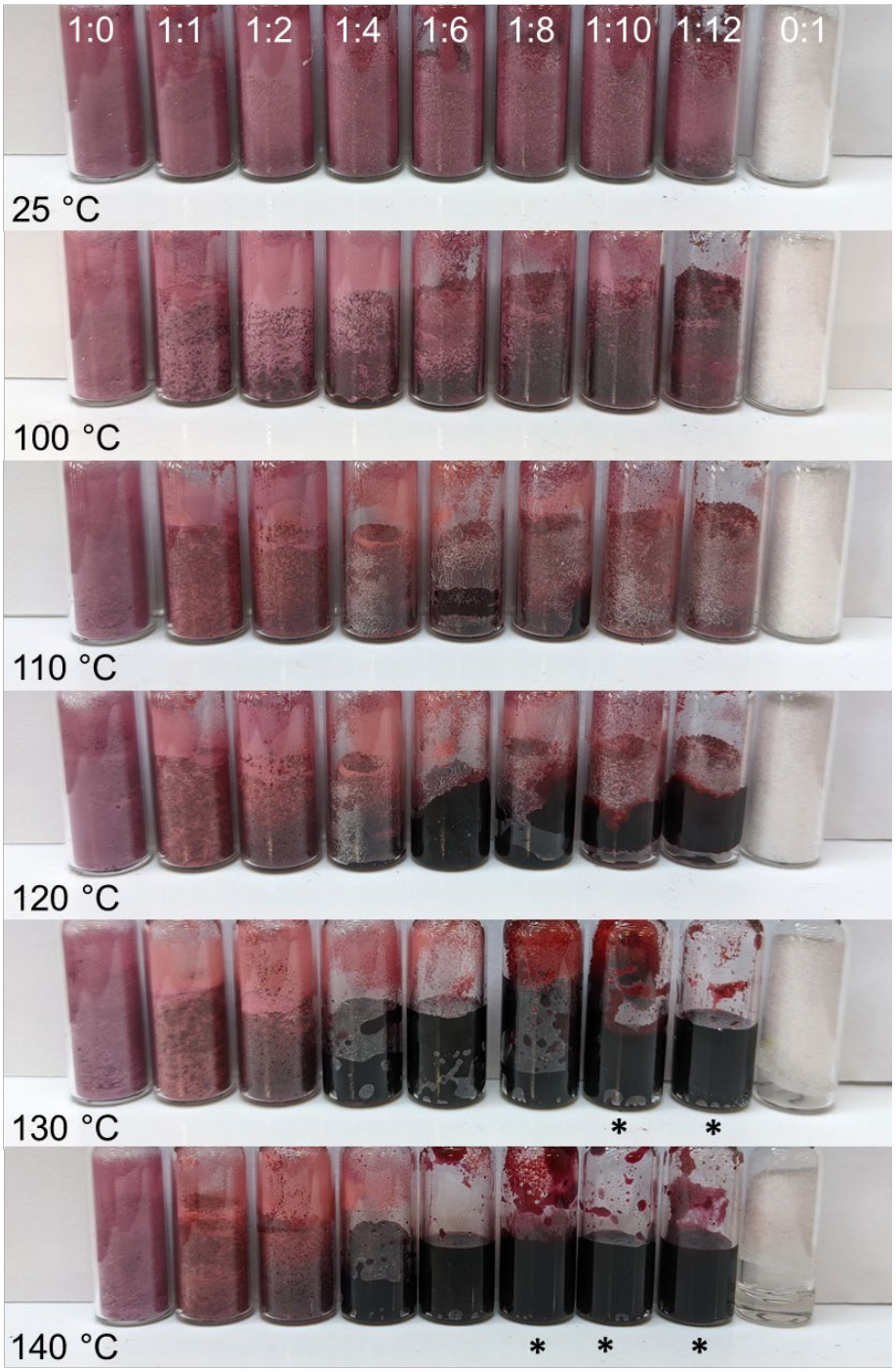

Fig. S6: Qualitative assessment of melting points of dry KCrPDTA:urea mixtures with increasing molar fractions of urea from left to right. Samples marked with a * are completely liquid. For reference, urea (melting point 133 °C) starts melting at a hotplate temperature of 130 – 140 °C.

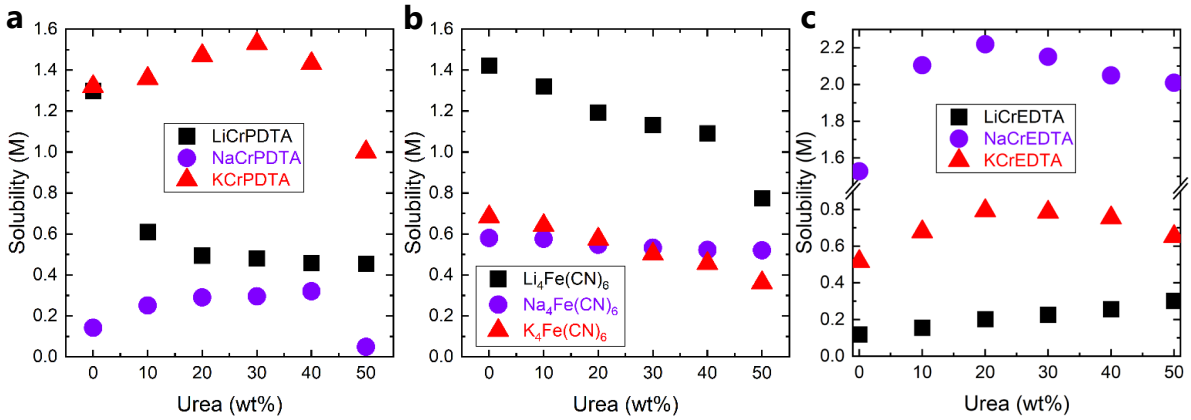

Fig. S7: Maximum solubility at room temperature of **a,** LiCrPDTA, NaCrPDTA, and KCrPDTA, **b,** $Li_4Fe(CN)_6$, $Na_4Fe(CN)_6$, and $K_4Fe(CN)_6$, and **c,** LiCrEDTA, NaCrEDTA, and KCrEDTA in aqueous urea solutions.

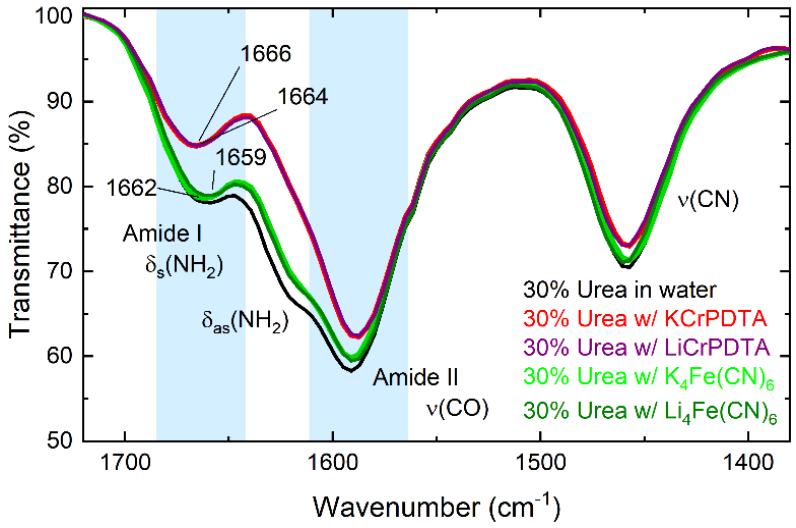

Fig. S8: **a,** IR spectra of 30% urea solutions with either 500 mM KCrPDTA or $K_4Fe(CN)_6$ or lithium analogues, respectively. The spectra of 500 mM respective salt in pure water were subtracted to obtain the urea signatures. Urea bands in 30% urea in water are shown for comparison.

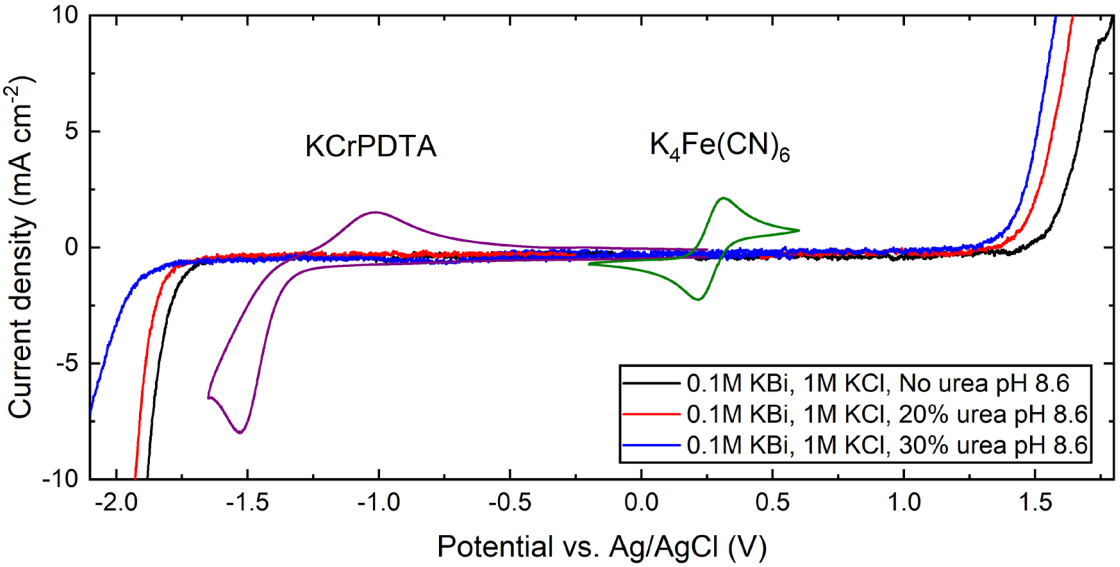

Fig. S9: Linear sweep voltammograms of buffered 1 M KCl solutions containing 0%, 20%, or 30% urea at pH 8.6 on glassy carbon electrodes. The scan rate was set to 10 mV s^{-1}. Cyclic voltammograms of KCrPDTA and $K_4Fe(CN)_6$ solutions are also shown. The current densities for the active material measurements were scaled for easier comparison.

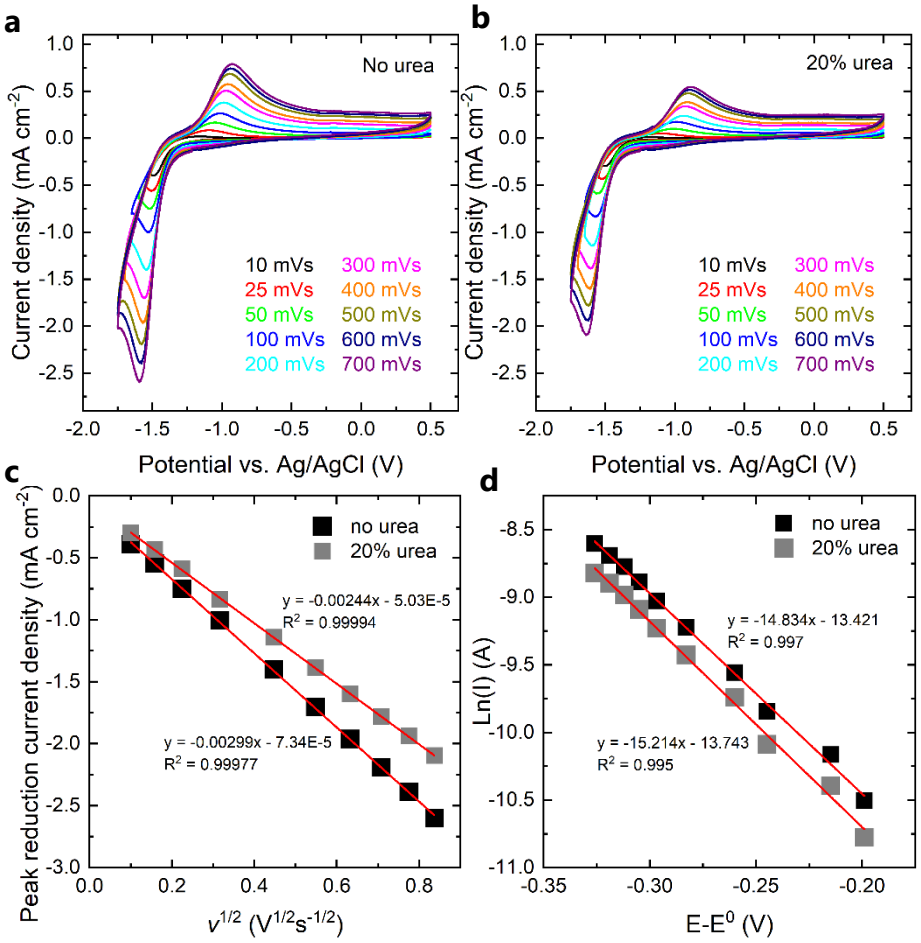

Fig. S10: Kinetic analysis of CrPDTA reduction with or without urea. **a,** Cyclic voltammograms of 5 mM KCrPDTA solutions in 0.1 M Borate buffer and 0.5 M KCl supporting electrolyte without or **b,** with 20% urea. Glassy carbon and Ag/AgCl electrodes were used as working or reference electrode, respectively. c, Peak reduction current versus the square root of the scan rate, with linear fit. **d,** Natural log of the peak reduction current versus the difference in potential between the voltage at the peak reduction current and the E^0 (−1.31 V vs. Ag/AgCl) of the reduction.

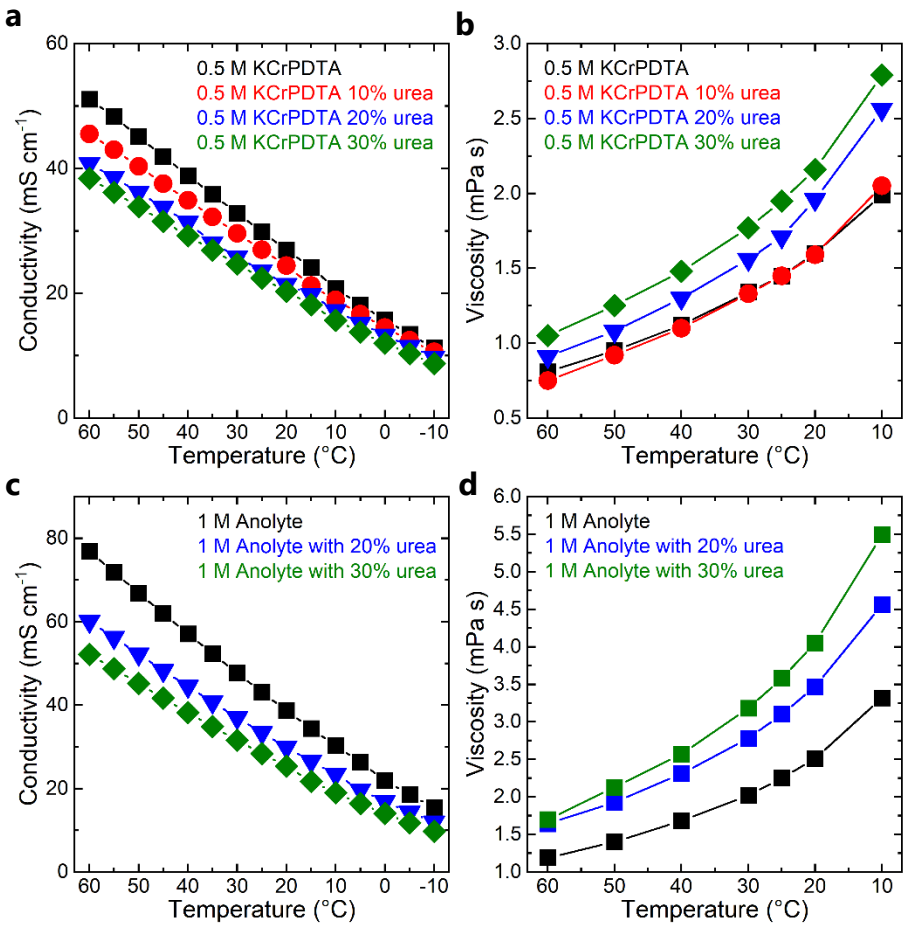

Fig. S11: **a,** Conductivity and **b,** viscosity of 0.5 M electrolytes with or without urea. **c,** Conductivity and **d,** viscosity of buffered 1 M KCrPDTA anolytes with or without urea.

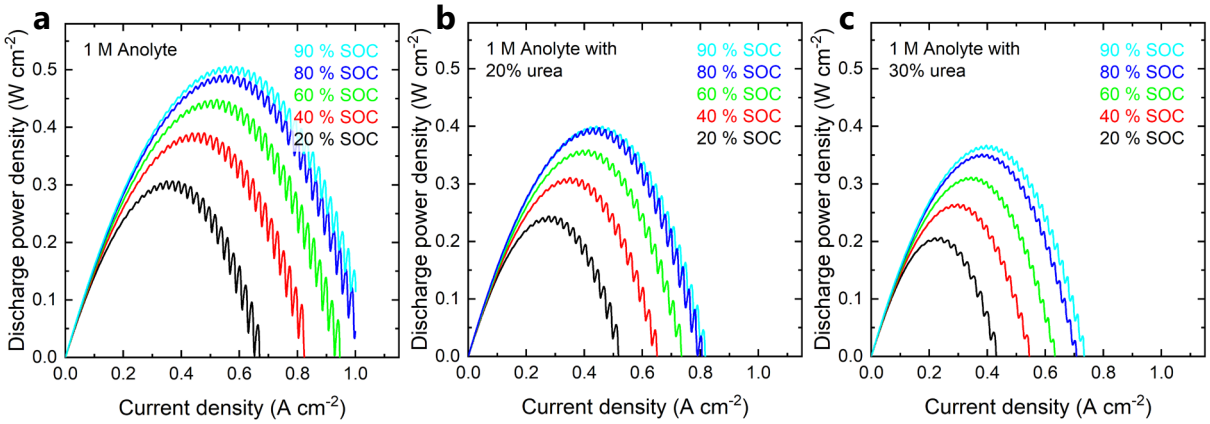

Fig. S12: Discharge power density versus current density at various states of charge using 1 M KCrPDTA anolytes containing **a,** no urea, **b,** 20% urea, or **c,** 30% urea. Oscillation of the current response is due to the pulsed electrolyte flow from the peristaltic pump.

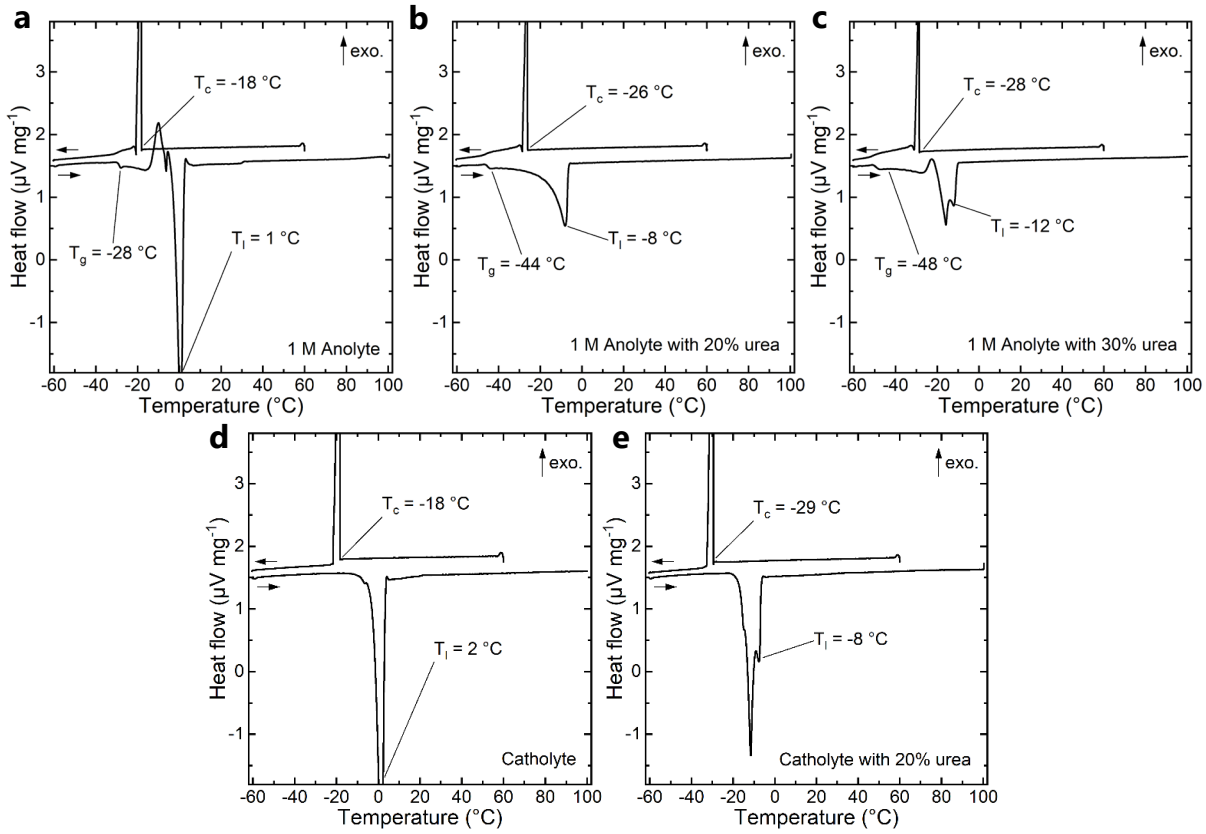

Fig. S13: **a,** Differential scanning calorimetry curves of 1 M KCrPDTA anolyte without urea and **b,** 20%, or **c,** 30% urea. **d,** 0.5 M $K_4Fe(CN)_6$ + 0.1M $K_3Fe(CN)_6$ catholyte without, and **e,** with 20% urea. Scans were recorded from 60 to −60 °C and back to 100 °C at a scan rate of 1 °C min^{-1}. All samples were mixed with a small amount of meso-carbon microbeads to provoke crystallization.

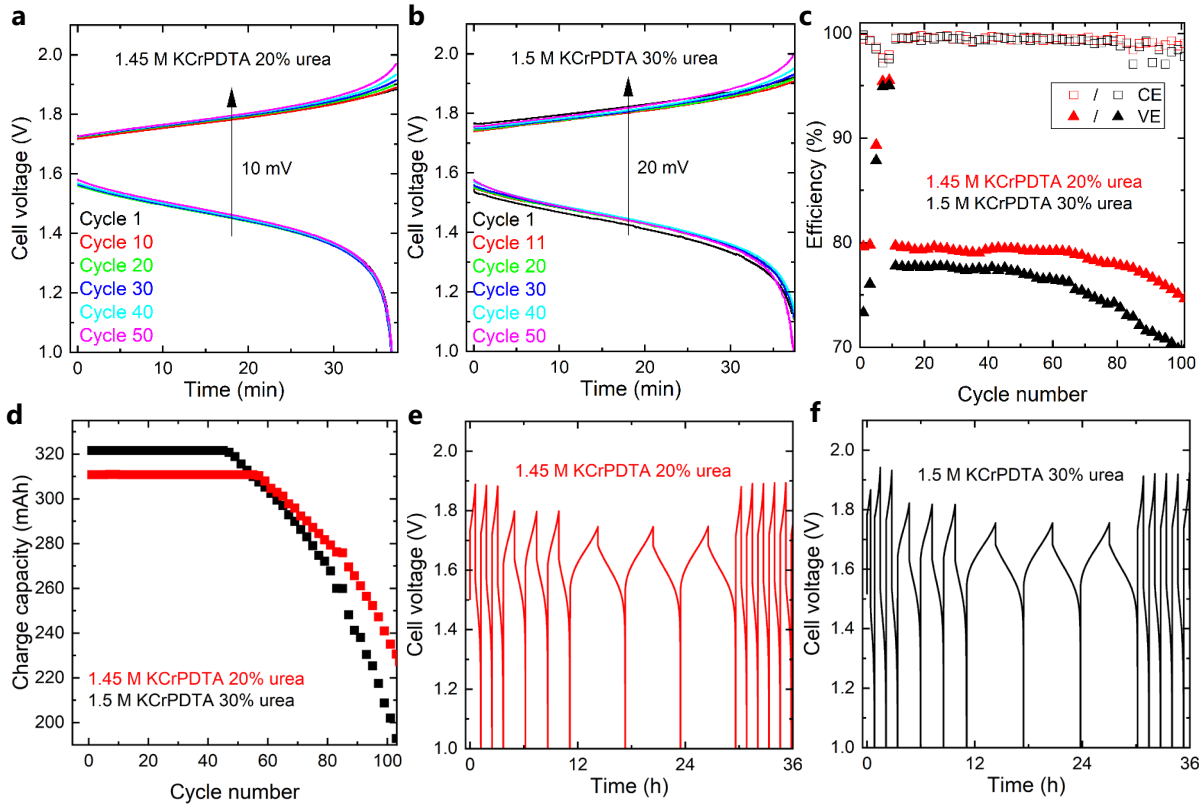

Fig. S14: Voltage profiles of the cells shown in Figure 5a using **a,e,** a 1.45 M KCrPDTA 20% urea anolyte, and **b,f,** a 1.5 M KCrPDTA 30% urea anolyte. **c,** Coulombic efficiency (CE) and voltage efficiency (VE) and **d,** charge capacity of the cells shown in Figure 5a for the full 100 cycles.

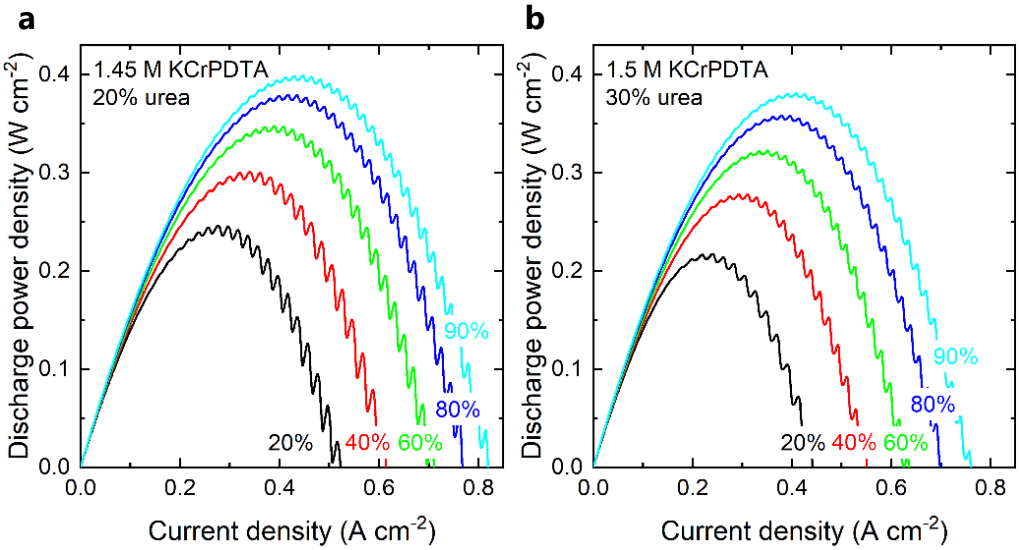

Fig. S15: Discharge power density versus current density at various states of charge using **a,** 1.45 M KCrPDTA 20% urea or **b,** 1.5 M 30% urea anolytes as for the cells shown in Figure 5. Oscillation of the current response is due to the pulsed electrolyte flow from the peristaltic pump.

Table S1: UV-Vis absorbance data for the examined complexes.

Compound	Wavelength [nm]	Molar absorptivity [M^{1-} L^{1-}]
$Fe(CN)_6^{4-}$	320	315 [2]
	420	1130 [2]
$CrPDTA^{1-}$	382	83 [3]
	506	116 [3]
$CrEDTA^{1-}$	390	113 [3]
	540	204 [3]
$CrCyDTA^{1-}$	390	97 [3,4]
	542	204 [3,4]

References

[1] Y.M. Jung, B. Czarnik-Matusewicz, S. Bin Kim, Characterization of concentration-dependent infrared spectral variations of urea aqueous solutions by principal component analysis and two-dimensional correlation spectroscopy, J. Phys. Chem. B. 108 (2004) 13008–13014. https://doi.org/https://doi.org/10.1021/jp049150c.

[2] M.H. Panckhurst, K.G. Woolmington, A spectrophotometric study of ionic association in aqueous solutions, Proc. R. Soc. London. Ser. A. Math. Phys. Sci. 244 (1958) 124–139.

[3] M. Hecht, F.A. Schultz, B. Speiser, Ligand structural effects on the electrochemistry of chromium (III) amino carboxylate complexes, Inorg. Chem. 35 (1996) 5555–5563. https://doi.org/https://doi.org/10.1021/ic960152o.

[4] N. Tanaka, K. Kanno, T. Tomita, A. Yamada, Synthesis and properties of sodium trans-1,2-cyclohexane-diaminetetraacetatochromate (III), Inorg. Nucl. Chem. Lett. 7 (1971) 953–956. https://doi.org/https://doi.org/10.1016/0020-1650(71)80008-9.