TAN, M., SAINI, G., STANZIONE, M., PANCHOLI, K., SAMPATHKUMAR, H., WALKER, M., PATTERSON, C., VASSALLI, M., NADEN, A., MAGDYSYUK, O., ARMSTRONG, R. and KUMAR, A. 2024. *Polyetherureas as aqueous binders for Li ion batteries*. [Preprint]. Hosted on ChemRxiv. Available from: https://doi.org/10.26434/chemrxiv-2024-mk39b

Polyetherureas as aqueous binders for Li ion batteries.

TAN, M., SAINI, G., STANZIONE, M., PANCHOLI, K., SAMPATHKUMAR, H., WALKER, M., PATTERSON, C., VASSALLI, M., NADEN, A., MAGDYSYUK, O., ARMSTRONG, R. and KUMAR, A.

2024

Polyetherureas as aqueous binders for Li ion Batteries

Mei Jun Tan,[a†] Garima Saini,[a†] Maximillian G. Stanzione,[a] Ketan Pancholi,[b] Harini Sampathkumar,[b] Matthew Walker,[c,d] Charlie Patterson,[d] Massimo Vassalli,[c,d] Aaron B. Naden,[a] Oxana V. Magdysyuk,[a] A. Robert Armstrong*,[a] Amit Kumar*[a]

[a]EaStCHEM, School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, KY169ST, UK.

[b]The Sir Ian Wood Building, Robert Gordon University, Garthdee Rd, Garthdee, Aberdeen, UK.

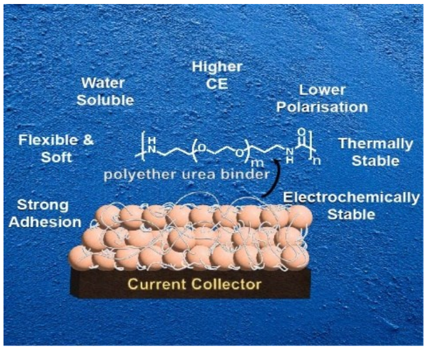
[c]Centre for the Cellular Microenvironment, Advanced Research Centre, University of Glasgow, Glasgow, UK.

[d]James Watt School of Engineering, University of Glasgow, Glasgow G12 8QQ, U.K.

* A. Robert Armstrong: ara@st-andrews.ac.uk

* Amit Kumar: ak336@st-andrews.ac.uk

ABSTRACT: We report here the application of polyetherureas as a new class of aqueous binder for the $LiFePO_4$ positive electrode material in lithium-ion batteries. Polyetherureas have been synthesized using a greener route (avoiding conventionally used toxic diisocyanate feedstock) by ruthenium-catalysed dehydrogenative coupling of polyethylene glycol diamine and methanol. The best binder performance was obtained when polyetherurea was used in combination with SBR (Styrene-Butadiene Rubber) exhibiting an initial coulombic efficiency of ~97% and a cell polarization of 30 mV. Remarkably, the combination of polyetherurea/SBR as a binder outperforms CMC (Carboxymethyl cellulose) which is a commonly used aqueous binder for lithium-ion batteries. Evidence of the involvement of polyetherureas on binder performance have been provided using IR spectroscopy, and scanning electron microscopy. Physical, electrochemical, and mechanical properties of the polyetherurea have been studied using TGA, DSC, powder XRD, cyclic voltammetry, nanoindentation, tensile testing and 180° peel test that shed light on why this polymer acts as a good binder.



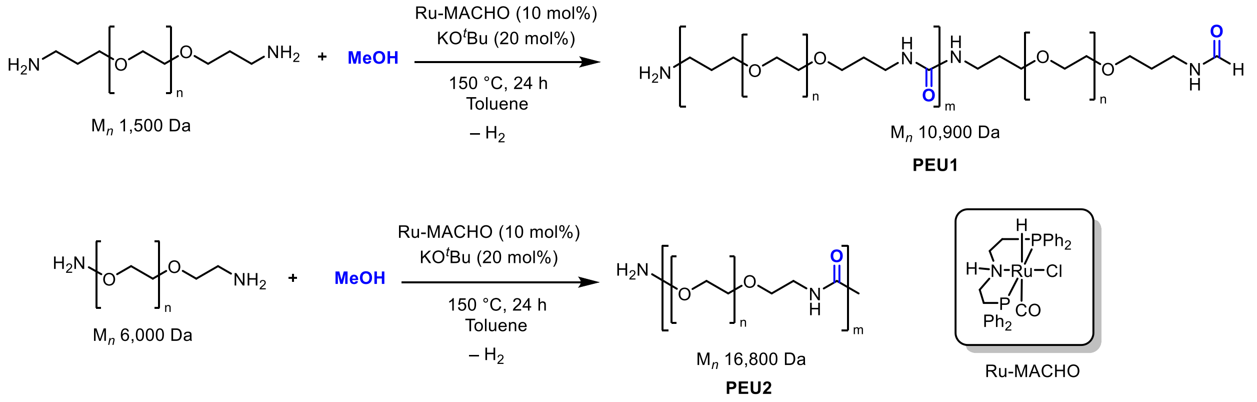
INTRODUCTION:

Binders are an important component of batteries that bind electrode components (e.g. active material, carbon additive) to each other and with the current collector.[1–4] Although they are used in a small quantity (2-5 wt%), they play various important roles in ensuring stable electrode structure and efficient mobility of ions. The multitasking need for binders requires them to bear several properties such as excellent (a) adhesion, (b) thermal and electrochemical stability, (c) mechanical properties, (d) dispersion performance (with other components), (e) swelling properties (with the electrolytes), and (f) ionic conductivity.[5–7] As a consequence, only a handful of materials have been successfully demonstrated as high-performance binders.[8–11] In current-state-of-the-art lithium-ion batteries (LIBs), Carboxy Methyl Cellulose (CMC) or Styrene-Butadiene Rubber (SBR) are generally used for anodes whereas for cathodes, non-aqueous binders such as PVDF (Polyvinylidene fluoride) are used. The use of non-aqueous binders for cathodes in LIBs has a few drawbacks such as the binder needs to be dissolved in toxic and flammable solvent such as N-methyl pyrrolidone (NMP) causing safety concerns. Additionally, removal of NMP in battery fabrication process takes significant energy due to its high boiling point (202 ^{o}C). Furthermore, NMP remains in the environment for extended periods and is known to emit significant amounts of greenhouse gases when burnt. Both the US Environmental Protection Agency,[12] and European Chemical Agency[13] have recently imposed significant restrictions on the use of NMP which are likely to be stricter in the future. These issues have led to significant interest in the development of aqueous binders for cathode materials for lithium-ion batteries in tandem with the development of water-stable electrodes. In fact, several polymers such as CMC,[14] polyacrylic acid (PAA),[15] chitosan,[16] alginate,[17] and guar gum[18] have been evaluated as aqueous binders for cathodes in lithium-ion batteries.[19–22] However, their performances are not as good as non-aqueous binders such as PVDF. Despite the technological advancements and development of several aqueous binders, there is not a 'one-size-fits-all' aqueous binder, and not all the existing aqueous binders are compatible with all materials. Therefore, it is of interest to develop new aqueous binders that could allow for the effective fabrication of batteries and demonstrate high performance.

In pursuit of new aqueous high-performance binders, we hypothesised that polyureas could potentially act as an efficient binder material due to their strong mechanical and adhesion properties arising due to polar functional groups.[23,24] Additionally, polyureas could have "rigid" (derived from aromatic groups) and "flexible" (derived from aliphatic chains) segments that can provide a higher degree of elasticity, tensile strength, and adhesion making them ideal for their use as a binder. In 2018, Sun et al. reported that a thin polyurea film could be utilised as an artificial SEI layer in Li-metal anodes through molecular-layer deposition.[25] According to their hypothesis, the presence of a large number of polar groups could also redistribute the Li-ion flux leading to uniform plating/stripping during the charging and discharging process. Considering the above-described properties of polyureas such as adhesivity, superior mechanical properties, and the recent development of polyurea to improve the SEI-layer, we hypothesised that polyureas could be used as an aqueous binder if a water-soluble polyurea could be made.

Polyureas are conventionally made from the reaction of diamines with diisocyanates which are known to be toxic. The precursor to make diisocyanates is phosgene gas which is even more hazardous to human health and the environment. Recent regulations have imposed stricter restrictions on the use and handling of diisocyanates and therefore opting for a non-isocyanate route to make a battery component would be desirable for making sustainable batteries.[26] We have recently demonstrated a new method of making polyureas from diamines and methanol feedstock which are much safer in comparison to using isocyanate feedstock.[27,28] Additionally, 100% renewable methanol is commercially available and can be made from the direct hydrogenation of CO_2 making such polyureas semi-renewable.[29] The polymerisation reaction is catalysed by a ruthenium or manganese pincer catalyst which dehydrogenatively couples methanol and amines to make formamides that subsequently react with amines to make urea derivatives and polyureas. Variations of catalytic conditions (e.g. precatalyst, base, temperature, solvent, time) can allow us to control the molecular weight which can influence the physical and mechanical properties of polyureas. Interestingly, we envisioned that diamines containing polyethyleneglycol linkages could allow us to make a water-soluble polyurea called "polyetherurea" which we hypothesized could be a potential candidate for use as an aqueous binder.

RESULTS AND DISCUSSION:



Scheme 1. Method used for the synthesis of polyetherureas used in this study.

We started our investigation by developing a catalytic protocol for the synthesis of polyetherurea from the dehydrogenative coupling of polyethyleneglycol diamine and methanol. The catalytic reaction was optimised through the variation of solvent, temperature, polyethyleneglycol diamine, amount of precatalyst, and base to result in high yield and molecular weight of the polyetherurea (see ESI, Table S1). The best yield of polyetherurea (~60%) was obtained using Ru-MACHO complex (10 mol%), and KO^tBu (20 mol%) as a catalyst in toluene at 150 ºC for 24 h (Scheme 1). The polyetherurea formed using this method from polyethyleneglycol propyletherdiamine exhibited an M_n of 10,900 Da and a polydispersity index of (Đ) of 1.4. The polyetherurea was further characterised by NMR and IR spectroscopy as well as MALDI-TOF mass spectrometry. This polyetherurea (PEU1) was tested on commercial $LiFePO_4$ (LFP) by galvanostatic cycling to monitor coulombic efficiency, charge, and discharge capacity, rate performance, and differential capacity analysis (dQ/dV). Interestingly, LFP with polyetherurea (PEU1) binder exhibited a promising discharge capacity of 148 mAh g^{-1} which is close to the theoretical discharge capacity of LFP. After 50 cycles, 98.9% of the initial capacity was retained (Figure 1). Furthermore, it showed a very high coulombic efficiency (99.2%) for 130 cycles while retaining a high specific capacity (148 mAh g^{-1}), and lower polarisation (0.05 V, Figures S35-S37, ESI). This retention in the discharge capacity and excellent coulombic efficiencies over the course of the cycling are desirable as they indicate no significant degradation of the battery.

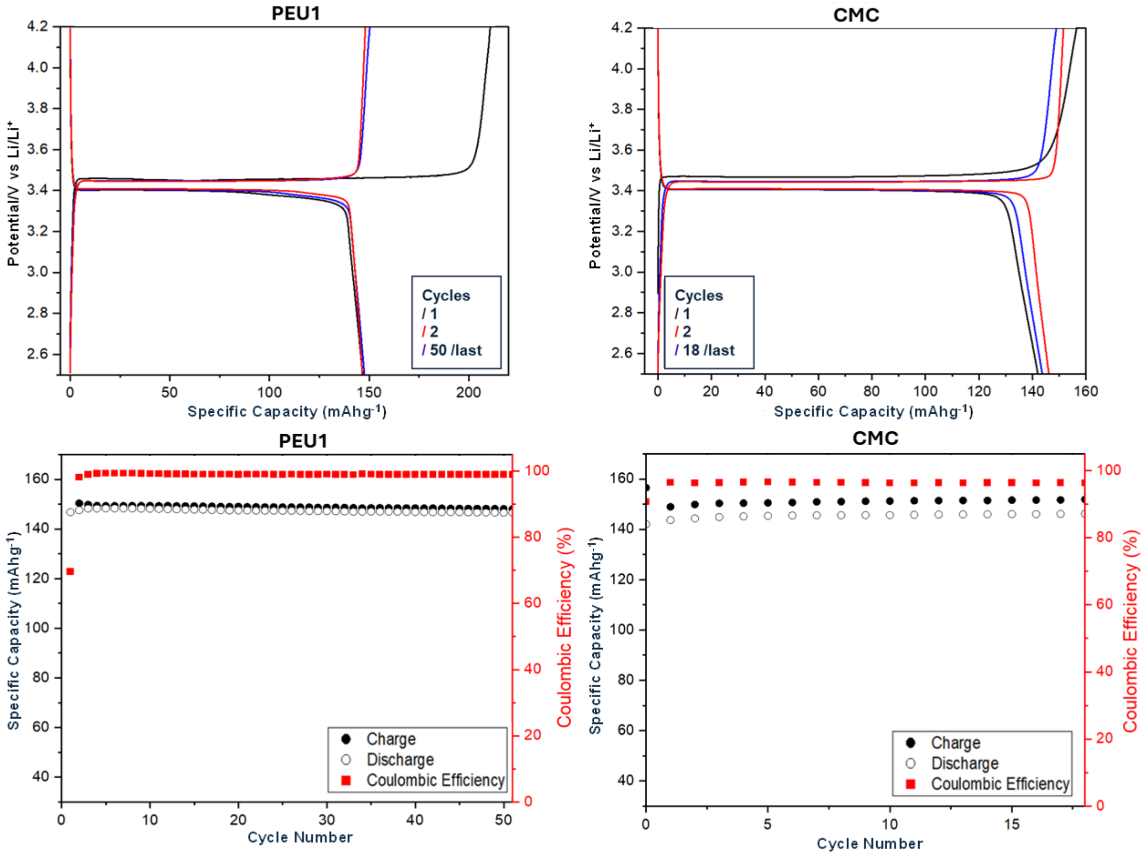


Figure 1. Specific capacity against potential (top), and against coulombic efficiency (bottom) for PEU1 and CMC with a 10 mA g^{-1} current density, cycled over the voltage window 2.5V to 4.2V.

We also compared the performance of PEU1 binder with that of CMC (carboxymethyl cellulose) which is a commonly used aqueous binder. CMC showed a maximum discharge capacity of 146 mAh g^{-1} and a capacity retention of 98.0%. In comparison, the polyetherurea (PEU1) exhibited a maximum discharge capacity of 148 mAh g^{-1} and a higher capacity retention of 98.9% over 130 cycles at the same rate of 10 mA g^{-1} over the voltage window 2.5-4.2 V. Although the CMC showed a higher initial coulombic efficiency (90.7% for CMC and 69.6% for PEU1), over successive cycling, the polyetherurea PEU1 exhibited higher coulombic efficiency of 99.2% compared to CMC's 96.5% indicating fewer parasitic side reactions leading to longer cycle life (Figure 1). The rate capability and differential capacity analysis, (shown in the ESI, Figures S22, S26, S34, S38) indicate similar charge and discharge capacities even at high current rates of 500 mA g^{-1} and comparable polarisation of 0.05 V for both the polyurea and CMC. This comparable performance is promising as it demonstrates that the polyetherurea can act as an aqueous binder equivalent to CMC. We speculate this could be because of polar functional groups (urea or alkoxy) present in the polyetherurea that could assist in the redistribution of lithium-ion flux.

SBR (styrene-butadiene rubber) is commonly added to CMC to form a composite that enhances the dispersive capabilities, flexibility, and binding strength and improves the electrochemical performance of electrodes.[7,30,31] We, therefore, studied the combination of polyetherurea (PEU1) with SBR (50:50) as an aqueous binder and compared its electrochemical performance against PEU1 for LFP. Comparatively, the PEU1+SBR has slightly higher charge and discharge capacities with stable discharge capacity throughout the cycles at 157 mAh g^{-1} (Figure 2). There is a considerably higher initial coulombic efficiency, of 96.9% (90.7% for CMC) when incorporating the SBR with the PEU1 which may be due to the absence of electrolyte oxidation or formation of a thinner SEI which does not have detrimental effects on the insertion and de-insertion process in later cycles which show 99.9% coulombic efficiency. In both samples (PEU1 and PEU1+SBR), there was limited polarisation which once again exhibits that the polyetherurea is a compatible binder with LFP. Furthermore, the dQ/dV plot showed that in the case of pure polyetherurea (PEU1), the oxidation/reduction peaks occur at 3.44/3.39 V which has a difference of 50 mV similar to that of CMC (see ESI, Figure S22). Comparatively, in the case of polyetherurea/SBR composite, the oxidation/reduction peaks occur at 3.44/3.41 V indicating an even smaller polarisation of 30 mV (see ESI, Fig. S42). These studies show that polyetherurea in combination with SBR performs as a better binder than pure polyetherurea and outperforms CMC as a binder.

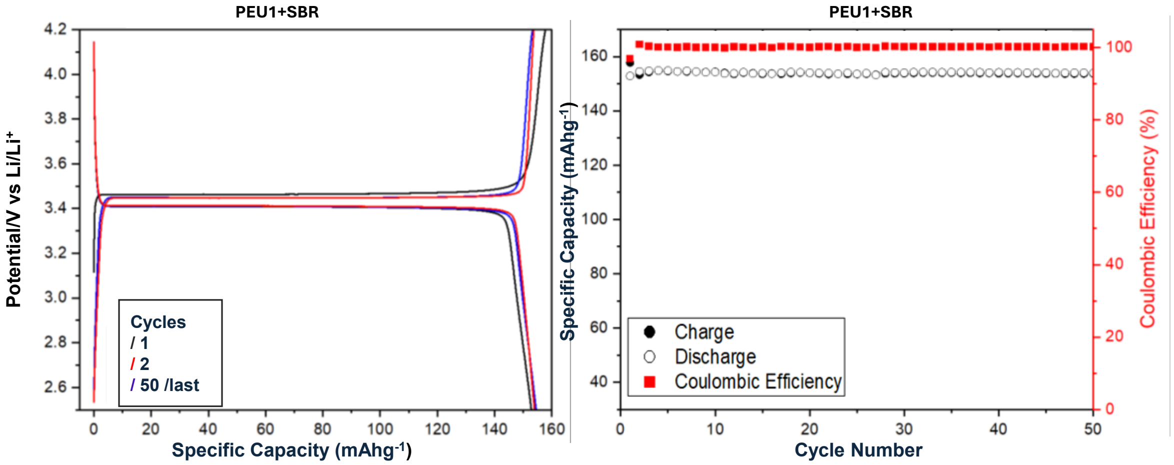


Figure 2. Specific capacity against potential (left), and against coulombic efficiency (right) for polyetherurea and SBR combination as a binder with a 10 mA g^{-1} current density, cycled over the voltage window 2.5V to 4.2V.

Encouraged by the performance of PEU1, we studied the effect of the nature of the polyetherurea on the specific capacity and coulombic efficiency. We compared the galvanostatic profile of PEU1 which is made from polyethyleneglycol bispropyl diamine of M_n = 1500 Da with the polyetherurea made from polyethyleneglycol diamine of M_n = 6000 Da (PEU2 in Scheme 1) under identical catalytic conditions (see ESI for the properties and characterization details of both the polyetherureas). The cycling data obtained from both polyetherureas exhibited the characteristic plateaus in both charge and discharge curves which indicate negligible difference in performance, and an unaffected redox mechanism (see ESI, section 1.6.5).

To probe if the urea functional group is important for binder applications, we compared PEU1/SBR with polyethylenglycol diamine/SBR which was used as a starting material to make polyetherurea. From the dQ/dV plots in Figure S52 (see ESI), the starting material (polyethyleneglycol diamine) showed a significantly lower capacity and pronounced polarisation compared to that of the polyetherurea (PEU1). Both plots showed a slightly higher first charge capacity, likely due to side reactions such as oxidation of the electrolyte. In the starting material (polyethylenglycol diamine/SBR), the oxidation/reduction peaks occur at 3.48/3.38 V which has a difference of 0.10 V, indicating a much larger polarisation than that of the PEU1/SBR which has a polarisation of 0.03 V. Furthermore, the starting material with SBR has a lower capacity of 92 mAh g^{-1} compared to that of 157 mAh g^{-1} in case of PEU1/SBR. This is likely because of the increased electrode resistance when the binder has inadequate adhesion to the electrode materials, possibly due to the lower degree of hydrogen bonding present in amine in comparison to urea. In the case of polyethyleneglycol diamine/SBR, there is a pronounced sloping behaviour in both the charging and discharging curves which is indicative of less well-defined phase transitions in the starting material potentially due to parasitic side reactions or increased resistance arising from poor electrode structure in later cycles. These studies suggest that the urea functionality is the positive contributor to the electrochemical performance and the presence of starting material (PEGdiamine) is detrimental to the electrochemical performance, particularly with regards to the lowered capacity and higher polarisation.

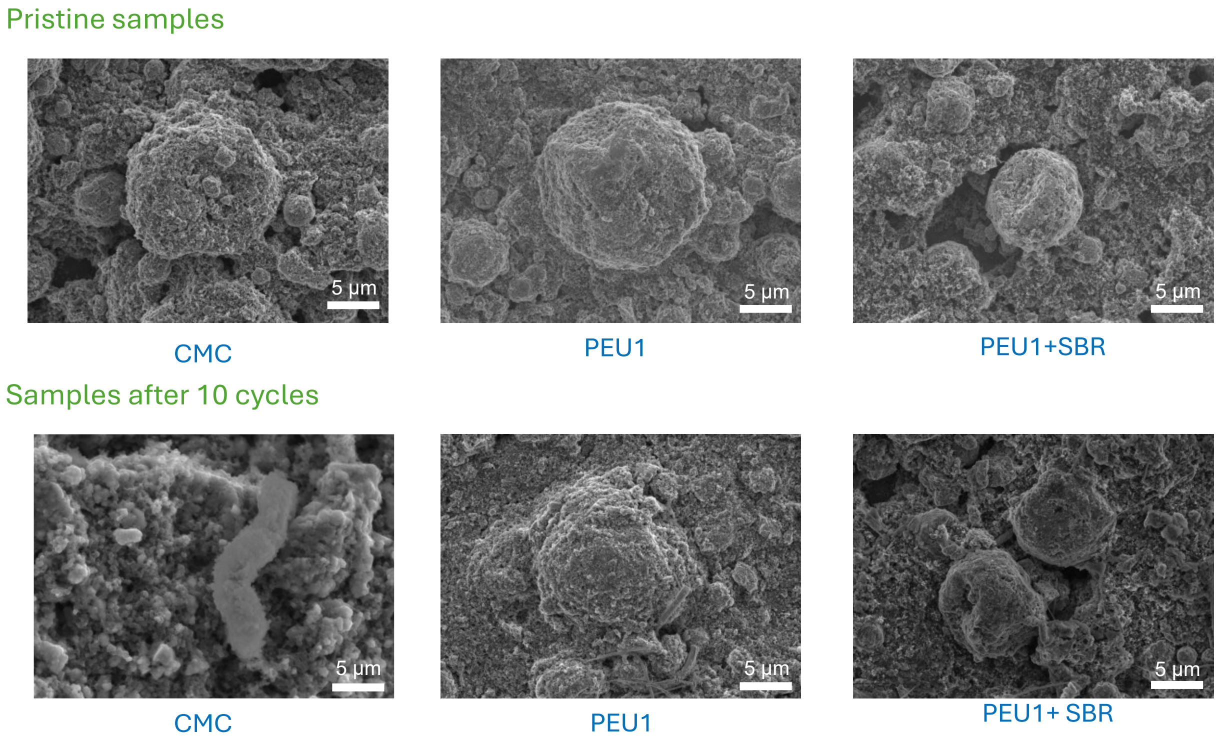


Figure 3. SEM images of cathode before and after galvanic cycles.

To investigate if the polyetherureas indeed are acting as binders, we analysed the electrode after 10 cycles using Scanning Electron Microscopy and IR spectroscopy. As seen in Figure 3, the morphology of the surface before and after galvanostatic cycling looks similar in the case of cells where PEU1 and PEU1+SBR were used as binders. No obvious cracking is observed suggesting that the polymer is acting as a good binder to keep the electrode intact. In contrast, the morphology appears to be changed in the case of the CMC binder. This supports our results of polyetherurea being a promising binder for LFP cathode material in lithium-ion batteries (Figure 3). Additionally, the IR spectrum before and after galvanostatic cycling appears the same qualitatively when

PEU1+SBR was used as a binder. However, some signals e.g. at 2885 cm^{-1} that would correspond to the N-H stretch of the polymer appear to diminish when just PEU1 was used as a binder whereas this is not the case for PEU1+SBR (Figure 4). This further confirms that polyetherurea+SBR is a more promising binder than just polyetherurea for lithium-ion batteries.

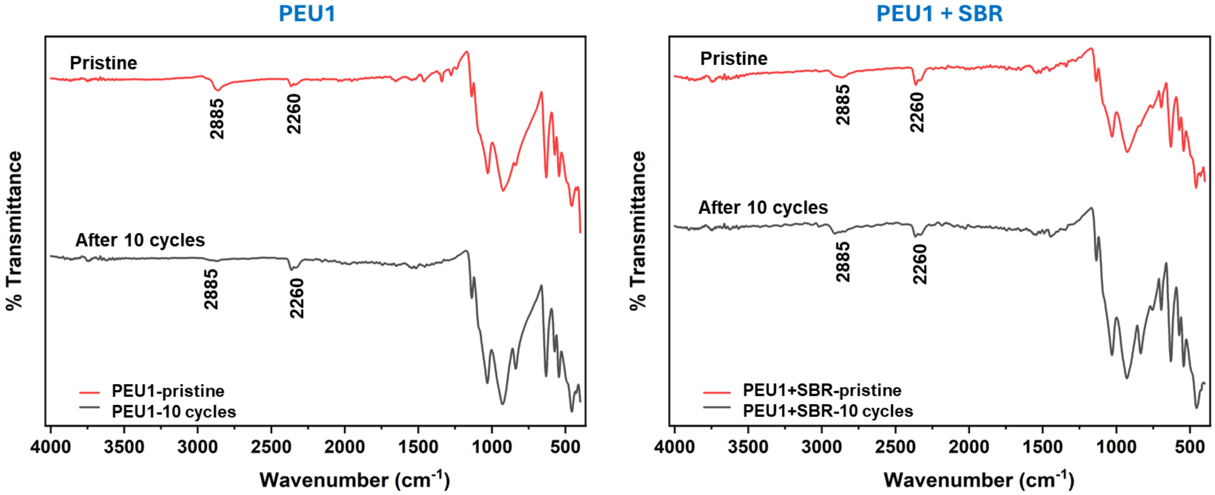


Figure 4. IR spectra of cathode before and after galvanic cycles.

We carried out further studies to understand the properties of polyetherurea (PEU1) that make it a good binder. Thermal stability of PEU1 was studied by the TGA (Thermogravimetric Analysis) that showed that PEU1 slowly decomposes between 220-400 ºC. The temperature of 90% mass loss was found to be 385 ºC which is slightly higher than that reported for CMC (350ºC).[32] This is suggestive of high thermal stability of the PEU1 which is an important criterion of a good binder. Additionally, the presence of higher crystallinity in a polymer such as CMC has shown enhanced performance of binder in the past due to increased adhesion and viscosity.[33] In line with this, the PXRD analysis of the PEU1 showed that the polymer is crystalline in nature with the crystallite size of ~70 nm and the unit cell volume of 1686 Å^3 (See ESI, Figure S15).

Another important property of a polymeric binder is its electrochemical inertness. This was probed by conducting cyclic voltammetry studies of half cells made using PEU1, PEU1+SBR, and CMC binders between a voltage window of 2.5V to 4.2V (Figure 5). In all these cases reversible redox processes were observed suggestive of the electrochemical stability of these materials. Additionally, a slightly higher polarisation was observed in case of PEU1 (reduction at 3.32 V and oxidation at 3.52 V, and $\Delta V = 200$ mV) in comparison to that of PEU1+SBR (reduction at 3.34 V and oxidation at 3.52 V, and $\Delta V = 180$ mV) suggestive of higher diffusion and lower resistance of Li^+ in case of PEU1+SBR. Furthermore, the relatively sharper shape in the case of PEU1+SBR is also suggestive of a single-step lithiation/delithiation process whereas this could be a more gradual process in the case when just PEU1 was used as a binder. These data suggest that PEU1+SBR is a better-performing binder than PEU1 as also discussed above. The redox behaviour in the case of PEU1+SBR was found to be similar to that of CMC binder with sharp shapes and polarisation of 170 mV (reduction at 3.35 V and oxidation at 3.52 V.)

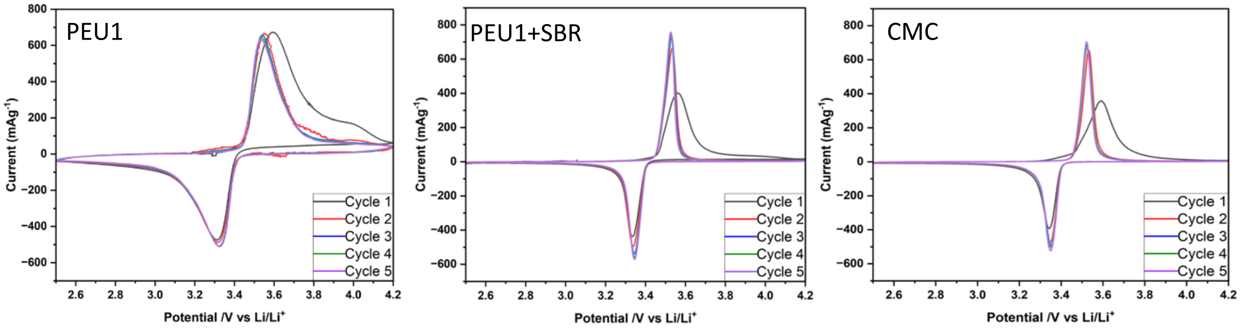


Figure 5. Cyclic voltammograms of the half cells containing different binders (5 cycles).

To get insights into the mechanical properties of binders, films of (2 mm thickness) of PEU1, SBR, and CMC were prepared and studied using the nanoindentation technique (Figure 6A). As shown in Figure 6C, the reduced elastic modulus of PEU1 (95 MPa) was found to be lower than those of SBR (189 MPa) and CMC (375 MPa). This could suggest that PEU1 is relatively more flexible and can change its shape and size considerably. This is beneficial for a binder as a flexible material can help prevent cracking and particle detachment during cycling. Similarly, the Rockell hardness number of PEU1 (20) was found to be lower than those of SBR (50), and CMC (93) suggesting that PEU1 is a softer material in comparison to SBR and CMC (Figure 6D). Performing the tensile testing on the PEU1 sample (stress/strain study, Figure 6B, see ESI for details) showed the yield strength to be 7.6 Mpa which is lower than that of CMC (~18 MPa) and similar to that of PVDF (<10 MPa).[34] This would suggest that in terms of elasticity PEU1 is similar to PVDF but inferior to CMC. The stress at failure (tensile strength) was measured to be (~18 MPa) for PEU1.

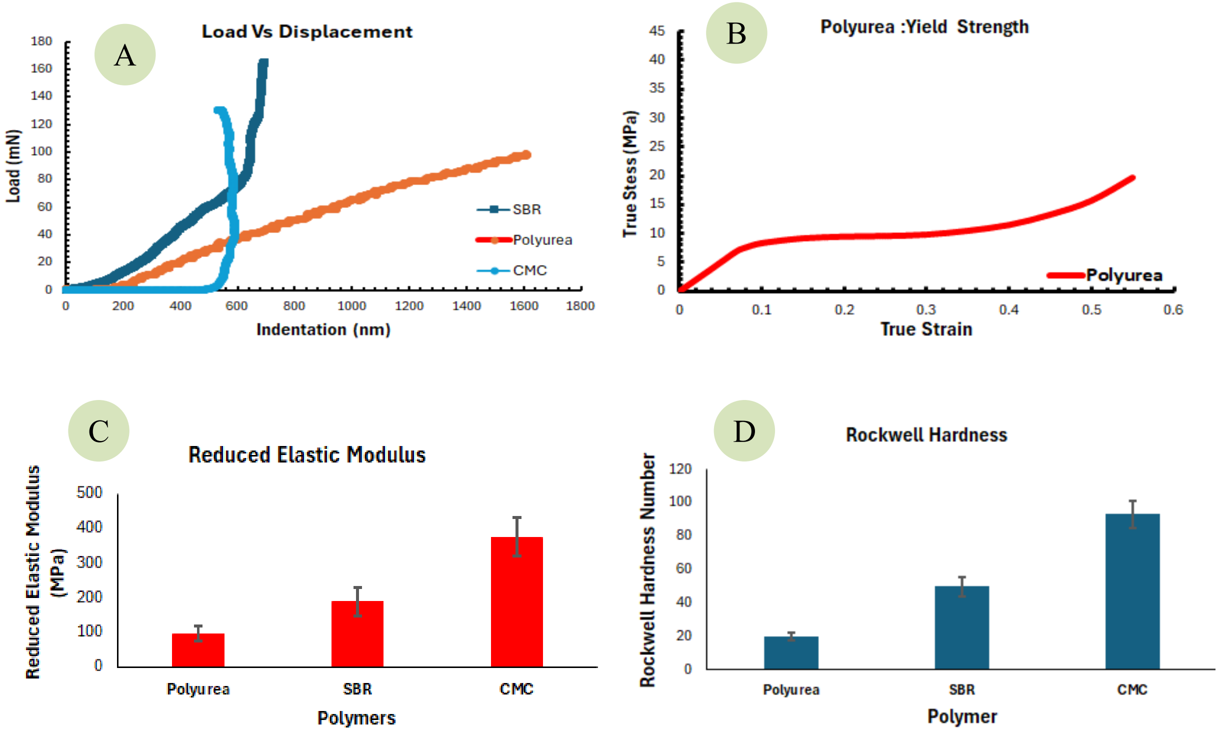


Figure 6. Load vs indentation curve from nanoindendation studies (A), and stress vs strain curve for PEU1 (B). Values of reduced elastic modulus (C) and Rockwell hardness numbers (D) for CMC, SBR, and PEU1.

Furthermore, the adhesive properties of these binders were studied by a 180° peel test (Figure 7). The adhesion force for CMC was found to be 0.7 N/cm which is only slightly lower than a reported value in the past (1.1 N/cm).[35] However, remarkably, the adhesive force in the case of PEU1 calculated using the same methodology was found to be 19.24 N/cm whereas the adhesive force for PEU1+SBR was found to be 18.5 N/cm. These data suggest that PEU1 has a much stronger adhesive property than CMC making it a desirable candidate for a high-performance binder. Polyureas are known to act as very strong adhesives and therefore these results are consistent with that.[36,37]

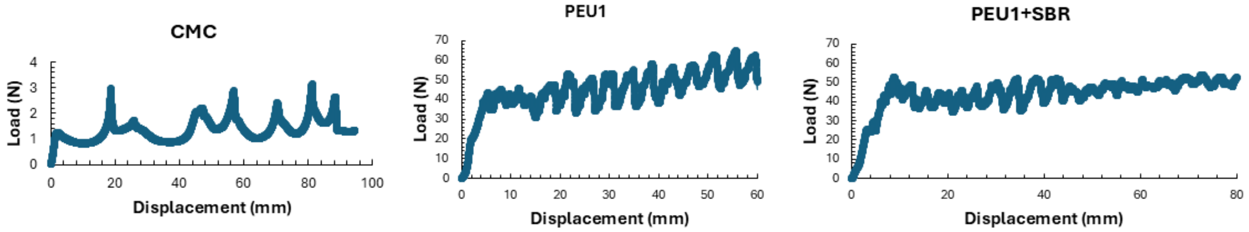


Figure 7. Load vs displacement plots from 180° peel test of binder electrodes.

CONCLUSION:

In conclusion, we have demonstrated polyetherurea as a new class of aqueous binder for lithium-ion batteries. The best results are obtained when polyetherurea is used in combination with SBR leading to a small polarisation of 30 mV and exhibiting a higher specific capacity of 157 mAhg^{-1} and a coulombic efficiency approaching 100% for LFP. In particular, the initial coulombic efficiency in case of PEU1+SBR (96.9) was found to be higher than that of CMC (90.7). Such attributes outperform CMC binder which is a commonly used aqueous binder for lithium-ion batteries. Further studies of the electrode material using SEM and IR spectroscopy suggest that indeed the polyetherurea (PEU1) keeps the cell intact acting as a suitable binder. Studying various properties of PEU1 revealed that PEU1 is thermally very stable (T_d = 385 °C), crystalline in nature, electrochemically stable (between 2.5V to 4.2V), and softer than CMC and SBR while exhibiting a moderate yield strength (7.5 MPa). Most remarkably, the PEU1 has significantly higher adhesion force in comparison to CMC or SBR. These properties clearly support the ability of PEU1 to act as a promising binder for lithium-ion batteries. A comparative summary of various properties and performance of PEU1 or PEU1+SBR with respect to CMC binder has been provided in Table 1.

Table 1. Comparison of properties/performance of PEU1/PEU1+SBR binder against those of CMC binder.

Property/Performance	**PEU1 or PEU1+SBR**	**CMC**
Initial Coulombic efficiency (ICE)*	69.6% for PEU1, 96.9% for PEU1+SBR	90.7%
Coulombic efficiency (after 18 cycles) *	99.2% for PEU1, 99.9% for PEU1+SBR	96.5%
Polarisation from dQ/dV study*	50 mV for PEU1, 30 mV for PEU1+SBR	50 mV
Discharge Specific Capacity*	148 mAg^{-1} for PEU1, 157 mAg^{-1} for PEU1+SBR	146 mAg^{-1}
Thermal decomposition	385 °C (90 % wt loss) for PEU1	350 °C[32]
Electrochemical stability (CV)	Reversible redox behaviour (ΔV = 200 mV for PEU1 and 180 mV for PEU1+SBR)	ΔV = 170 mV
Reduced elastic modulus	95 MPA (PEU1)	375 MPa
Rockwell hardness number	20 (PEU1)	93
Yield strength	7.6 MPa (PEU1)	18 MPa
Adhesion force	19.24 N/cm	0.7 N/cm

*at 10 mA g^{-1} current density, cycled over the voltage window 2.5V to 4.2V.

Thus, we believe that the proof of concept reported here opens up new avenues to use polyetherureas as aqueous binders with various electrode materials in different types of alkali metal batteries.

ACKNOWLEDGEMENTS:

This research is funded by a UKRI Future Leaders Fellowship (MR/ W007460/1) and an EPSRC grant (EP/Y005449/1).

KEYWORDS: Li ion batteries, polymers, ruthenium, pincer, dehydrogenation

REFERENCES:

(1) Zou, F.; Manthiram, A. A Review of the Design of Advanced Binders for High-Performance Batteries. *Adv Energy Mater* **2020**, *10* (45), 2002508. https://doi.org/https://doi.org/10.1002/aenm.202002508.

(2) Xing, J.; Bliznakov, S.; Bonville, L.; Oljaca, M.; Maric, R. A Review of Nonaqueous Electrolytes, Binders, and Separators for Lithium-Ion Batteries. *Electrochemical Energy Reviews* **2022**, *5* (4), 14. https://doi.org/10.1007/s41918-022-00131-z.

(3) Wang, Y.-B.; Yang, Q.; Guo, X.; Yang, S.; Chen, A.; Liang, G.-J.; Zhi, C.-Y. Strategies of Binder Design for High-Performance Lithium-Ion Batteries: A Mini Review. *Rare Metals* **2022**, *41* (3), 745–761. https://doi.org/10.1007/s12598-021-01816-y.

(4) Yoon, J.; Lee, J.; Kim, H.; Kim, J.; Jin, H.-J. Polymeric Binder Design for Sustainable Lithium-Ion Battery Chemistry. *Polymers*. 2024. https://doi.org/10.3390/polym16020254.

(5) Chen, H.; Ling, M.; Hencz, L.; Ling, H. Y.; Li, G.; Lin, Z.; Liu, G.; Zhang, S. Exploring Chemical, Mechanical, and Electrical Functionalities of Binders for Advanced Energy-Storage Devices. *Chem Rev* **2018**, *118* (18), 8936–8982. https://doi.org/10.1021/acs.chemrev.8b00241.

(6) He, Q.; Ning, J.; Chen, H.; Jiang, Z.; Wang, J.; Chen, D.; Zhao, C.; Liu, Z.; Perepichka, I. F.; Meng, H.; Huang, W. Achievements, Challenges, and Perspectives in the Design of Polymer Binders for Advanced Lithium-Ion Batteries. *Chem Soc Rev* **2024**, *53* (13), 7091–7157. https://doi.org/10.1039/D4CS00366G.

(7) Chen, B.; Zhang, Z.; Xiao, M.; Wang, S.; Huang, S.; Han, D.; Meng, Y. Polymeric Binders Used in Lithium Ion Batteries: Actualities, Strategies and Trends. *ChemElectroChem* **2024**, *11* (14), e202300651. https://doi.org/https://doi.org/10.1002/celc.202300651.

(8) Morris, M. A.; An, H.; Lutkenhaus, J. L.; Epps, T. H. Harnessing the Power of Plastics: Nanostructured Polymer Systems in Lithium-Ion Batteries. *ACS Energy Lett* **2017**, *2* (8), 1919–1936. https://doi.org/10.1021/ACSENERGYLETT.7B00368/ASSET/IMAGES/MEDIUM/NZ-2017-003689_0009.GIF.

(9) Hong, S. B.; Jang, Y. R.; Kim, H.; Jung, Y. C.; Shin, G.; Hah, H. J.; Cho, W.; Sun, Y. K.; Kim, D. W. Wet-Processable Binder in Composite Cathode for High Energy Density All-Solid-State Lithium Batteries. *Adv Energy Mater* **2024**, *14* (35), 2400802. https://doi.org/10.1002/AENM.202400802.

(10) Ming, J.; Ming, H.; Kwak, W. J.; Shin, C.; Zheng, J.; Sun, Y. K. The Binder Effect on an Oxide-Based Anode in Lithium and Sodium-Ion Battery Applications: The Fastest Way to Ultrahigh Performance. *Chemical Communications* **2014**, *50* (87), 13307–13310. https://doi.org/10.1039/C4CC02657H.

(11) Ma, Y.; Ma, J.; Cui, G. Small Things Make Big Deal: Powerful Binders of Lithium Batteries and Post-Lithium Batteries. *Energy Storage Mater* **2019**, *20*, 146–175. https://doi.org/10.1016/J.ENSM.2018.11.013.

(12) Https://cen.acs.org/policy/chemical-regulation/EPA-seeks-limits-NMP-use/102/i18.

(13) https://echa.europa.eu/substance-information/-/substanceinfo/100.011.662.

(14) Doberdò, I.; Löffler, N.; Laszczynski, N.; Cericola, D.; Penazzi, N.; Bodoardo, S.; Kim, G. T.; Passerini, S. Enabling Aqueous Binders for Lithium Battery Cathodes – Carbon Coating of Aluminum Current Collector. *J Power Sources* **2014**, *248*, 1000–1006. https://doi.org/10.1016/J.JPOWSOUR.2013.10.039.

(15) Cai, Z. P.; Liang, Y.; Li, W. S.; Xing, L. D.; Liao, Y. H. Preparation and Performances of LiFePO4 Cathode in Aqueous Solvent with Polyacrylic Acid as a Binder. *J Power Sources* **2009**, *189* (1), 547–551. https://doi.org/10.1016/J.JPOWSOUR.2008.10.040.

(16) Zhong, H.; He, A.; Lu, J.; Sun, M.; He, J.; Zhang, L. Carboxymethyl Chitosan/Conducting Polymer as Water-Soluble Composite Binder for LiFePO4 Cathode in Lithium Ion Batteries. *J Power Sources* **2016**, *336*, 107–114. https://doi.org/10.1016/J.JPOWSOUR.2016.10.041.

(17) Zhang, S. J.; Deng, Y. P.; Wu, Q. H.; Zhou, Y.; Li, J. T.; Wu, Z. Y.; Yin, Z. W.; Lu, Y. Q.; Shen, C. H.; Huang, L.; Sun, S. G. Sodium-Alginate-Based Binders for Lithium-Rich Cathode Materials in Lithium-Ion Batteries to Suppress Voltage and Capacity Fading. *ChemElectroChem* **2018**, *5* (9), 1321–1329. https://doi.org/10.1002/CELC.201701358.

(18) Kaur, S.; Santra, S. Application of Guar Gum and Its Derivatives as Green Binder/Separator for Advanced Lithium-Ion Batteries. *ChemistryOpen* **2022**, *11* (2), e202100209. https://doi.org/10.1002/OPEN.202100209.

(19) Lingappan, N.; Kong, L.; Pecht, M. The Significance of Aqueous Binders in Lithium-Ion Batteries. *Renewable and Sustainable Energy Reviews* **2021**, *147*, 111227. https://doi.org/https://doi.org/10.1016/j.rser.2021.111227.

(20) Dobryden, I.; Montanari, C.; Bhattacharjya, D.; Aydin, J.; Ahniyaz, A. Bio-Based Binder Development for Lithium-Ion Batteries. *Materials*. 2023. https://doi.org/10.3390/ma16165553.

(21) Zhang, X.; Ge, X.; Shen, Z.; Ma, H.; Wang, J.; Wang, S.; Liu, L.; Liu, B.; Liu, L.; Zhao, Y. Green Water-Based Binders for LiFePO4/C Cathodes in Li-Ion Batteries: A Comparative Study. *New Journal of Chemistry* **2021**, *45* (22), 9846–9855. https://doi.org/10.1039/D1NJ01208H.

(22) Bresser, D.; Buchholz, D.; Moretti, A.; Varzi, A.; Passerini, S. Alternative Binders for Sustainable Electrochemical Energy Storage – the Transition to Aqueous Electrode Processing and Bio-Derived Polymers. *Energy Environ Sci* **2018**, *11* (11), 3096–3127. https://doi.org/10.1039/C8EE00640G.

(23) Zhang, R.; Huang, W.; Lyu, P.; Yan, S.; Wang, X.; Ju, J. Polyurea for Blast and Impact Protection: A Review. *Polymers*. 2022. https://doi.org/10.3390/polym14132670.

(24) Shojaei, B.; Najafi, M.; Yazdanbakhsh, A.; Abtahi, M.; Zhang, C. A Review on the Applications of Polyurea in the Construction Industry. *Polym Adv Technol* **2021**, *32* (8), 2797–2812. https://doi.org/https://doi.org/10.1002/pat.5277.

(25) Sun, Y.; Zhao, Y.; Wang, J.; Liang, J.; Wang, C.; Sun, Q.; Lin, X.; Adair, K. R.; Luo, J.; Wang, D.; Li, R.; Cai, M.; Sham, T.-K.; Sun, X. A Novel Organic "Polyurea" Thin Film for Ultralong-Life Lithium-Metal Anodes via Molecular-Layer Deposition. *Adv. Mat.* **2019**, *31* (4), 1806541. https://doi.org/https://doi.org/10.1002/adma.201806541.

(26) Https://www.isopa.org/the-eu-introduces-mandatory-training-of-diisocyanates-workers-from-24-august-2023-in-new-reach-restriction/.

(27) Owen, A. E.; Preiss, A.; McLuskie, A.; Gao, C.; Peters, G.; Bühl, M.; Kumar, A. Manganese-Catalyzed Dehydrogenative Synthesis of Urea Derivatives and Polyureas. *ACS Catal* **2022**, *12* (12), 6923–6933. https://doi.org/10.1021/acscatal.2c00850.

(28) Kumar, A.; Armstrong, D.; Peters, G.; Nagala, M.; Shirran, S. Direct Synthesis of Polyureas from the Dehydrogenative Coupling of Diamines and Methanol. *Chem.Commun.* **2021**, 57, 6153-6156. https://doi.org/10.1039/D1CC01121A.

(29) Roode-Gutzmer, Q. I.; Kaiser, D.; Bertau, M. Renewable Methanol Synthesis. *ChemBioEng Reviews* **2019**, *6* (6), 209–236. https://doi.org/10.1002/cben.201900012.

(30) Hofmann, K.; Hegde, A. D.; Liu-Theato, X.; Gordon, R.; Smith, A.; Willenbacher, N. Effect of Mechanical Properties on Processing Behavior and Electrochemical Performance of Aqueous Processed Graphite Anodes for Lithium-Ion Batteries. *J Power Sources* **2024**, *593*, 233996. https://doi.org/https://doi.org/10.1016/j.jpowsour.2023.233996.

(31) Wang, R.; Feng, L.; Yang, W.; Zhang, Y.; Zhang, Y.; Bai, W.; Liu, B.; Zhang, W.; Chuan, Y.; Zheng, Z.; Guan, H. Effect of Different Binders on the Electrochemical Performance of Metal Oxide Anode for Lithium-Ion Batteries. *Nanoscale Res Lett* **2017**, *12* (1), 575. https://doi.org/10.1186/s11671-017-2348-6.

(32) de Britto, D.; Assis, O. B. G. Thermal Degradation of Carboxymethylcellulose in Different Salty Forms. *Thermochim Acta* **2009**, *494* (1), 115–122. https://doi.org/https://doi.org/10.1016/j.tca.2009.04.028.

(33) Nishanth, J.; Singh, D.; Panja, S.; Chandran, T. M.; Brajesh, K.; Omar, S.; Nalwa, K. S. Investigating the Influence of PVDF Binder Crystallinity on the Performance of LiFePO4 Cathode in Li-Ion Batteries. *Oxford Open Materials Science* **2023**, *3* (1), itad019. https://doi.org/10.1093/oxfmat/itad019.

(34) Li, J.; Lewis, R. B.; Dahn, J. R. Sodium Carboxymethyl Cellulose: A Potential Binder for Si Negative Electrodes for Li-Ion Batteries. *Electrochemical and Solid-State Letters* **2007**, *10* (2), A17. https://doi.org/10.1149/1.2398725.

(35) Qin, T.; Yang, H.; Li, Q.; Yu, X.; Li, H. Design of Functional Binders for High-Specific-Energy Lithium-Ion Batteries: From Molecular Structure to Electrode Properties. *Industrial Chemistry & Materials* **2024**, *2* (2), 191–225. https://doi.org/10.1039/D3IM00089C.

(36) Han, L.; Xu, J.; Li, L.; Lin, J.; Ren, K.; Yang, K.; Wu, A.; Zhang, R. In Situ Adhesive and Crack Detectable Polyurea Adhesive at Extremely Low Temperatures. *Macromolecules* **2024**, *57* (17), 8432–8444. https://doi.org/10.1021/acs.macromol.4c01430.

(37) Yang, H.; Du, G.; Li, Z.; Ran, X.; Zhou, X.; Li, T.; Gao, W.; Li, J.; Lei, H.; Yang, L. Superstrong Adhesive of Isocyanate-Free Polyurea with a Branched Structure. *ACS Appl Polym Mater* **2021**, *3* (3), 1638–1651. https://doi.org/10.1021/acsapm.1c00056.