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## **Cross-linking Effects on Performance Metrics of Phenazine-Based Polymer Cathodes**

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**Abstract:** Developing cathodes that can support high chargedischarge rates would improve the power density of lithium ion batteries. Herein, we report the development of high power cathodes, without sacrificing energy density. *N*,*N*-Diphenyl phenazine was identified as a promising charge storage center by electrochemical studies due to its reversible, fast electron transfer at high potentials. By incorporating the phenazine redox units in a cross-linked network, a high capacity (223 mAh/g), high voltage (3.45 V vs Li/Li<sup>+</sup>) cathode material was achieved. Optimized cross-linked materials are able to deliver reversible capacities as high as 220 mAh g<sup>-1</sup> at 120 C with minimal degradation over 1000 cycles. The work presented here highlights the fast ionic transport and rate capabilities of amorphous, organic materials and demonstrates their potential as high energy and power density materials for next generation electrical energy storage technologies.

#### Introduction

Electrification of transportation is expected to play a critical role in curbing carbon emissions and utilizing renewable energy. Recently, the US Department of Energy has set an initial target of 15 minute battery charging times to advance the market penetration of electric vehicles.<sup>[1]</sup> Currently, capacitors are the only electrical energy storage systems capable of stably delivering and sustaining these rates, due to their fast rates of charge storage.<sup>[2]</sup> However, capacitors lack faradaic reactions resulting in low energy densities when compared to batteries, compromising the range of electric vehicles. Current battery materials have seen significant improvements in energy density and lifetime over the past decade. However, the diffusive nature of the energy storage processes continues to limit their rate performance.<sup>[3]</sup> Thus, it is necessary to increase the charge and

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[†] These authors contributed equally to this work. ion transport dynamics to improve the power density of these devices.

During charge and discharge, crystalline inorganic cathodes undergo kinetically slow (de)intercalation events which limit the rate of ion diffusion. In amorphous organic materials, charge balancing counter ion transport can be dramatically enhanced due to the relatively weak intermolecular forces within the materials.<sup>[4,5]</sup> This enables amorphous, organic materials to accommodate fast ion transport, resulting in faster charging and discharging rates. However, designing amorphous, organic materials that can deliver high power density without sacrificing operating voltage, capacity, or stability has proven challenging.<sup>[6-8]</sup>

Cross-linking in binders, electrolytes, and electrode materials, provides greater resistance to dissolution, improved stability, and supports an amorphous nature to increase ion conductivity.[9-13] We hypothesized that the morphology of a redox active polymer could be optimized by strategically tuning the cross-linking density. Cross-linking can disrupt ordering and restrict polymer mobility, ensuring an open, amorphous structure even in a swelled state. Recently, we reported on a cathode material which utilized 3,7diamino-substituted phenothiazines as charge storage elements.<sup>[14]</sup> In that study, cross-linking of a linear energy storage polymer lead to improved stability upon cycling, higher discharge capacities, and improved rate performance. Unfortunately, the material exhibited poor capacity retention upon cycling, a likely consequence of polymer degradation. In an effort to better understand the effects of cross-linking, a polymer containing more stable redox centers was necessary. Substituted phenazine structures, specifically N,N'-diphenylphenazine (1), were identified as a promising class of charge storage motifs through electrochemical screening/analysis of phenazine-based small molecule analogues.

In recent years, phenazine has been identified as a promising charge storage unit in cathodes, capacitors, and as redox flow catholyte.<sup>[15-24]</sup> Recent work on phenazine-based p-type energy materials has been led by Zhang and coworkers, who became interested in **1** for its ability to improve charge delocalization about the dihydrophenazine unit.<sup>[23,24]</sup> In a collaborative effort with Zhou, they demonstrated the utility of a crystalline phenazine-based bipolar molecule in a dual-ion symmetric battery, with full cell capacities as high as 57 mAh g<sup>-1</sup>. Additionally, they demonstrated the potential of a linear polymer containing phenazine units as a high voltage cathode material, delivering 65 mAh g<sup>-1</sup> at a discharge rate of 5 C. However, in neither accounts, were high C-rates reported.

Through ternary copolymerizations, we have synthesized cross-linked polymers based around substituted phenazines and studied the effects of cross-linking on their electrochemical performance as amorphous cathode materials. These crosslinked phenazine-based polymers delivered energy densities competitive with commercial cathodes while providing

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dramatically enhanced power densities. By optimizing the crosslinking density in these materials, we developed a cathode material that can deliver a remarkable capacity of 220 mAh/g at 120 C with minimal loss in capacity.

#### **Results and Discussion**

#### Electrochemical optimization of redox storage unit

The electrochemical properties of the redox active unit within a material can dictate many of the performance metrics of the resulting cathode, including operating voltage, cathode stability, and rate capabilities. Thus, careful design and electrochemical analysis of the redox unit, as a small molecule, can enable ideal performance in the material. Alkylation and arylation of phenazine, leads to improved kinetic and thermodynamic performance metrics over unsubstituted phenazine. The modified N,N'disubstituted phenazine units cycle between a neutral and dicationic state, belonging to a class known as p-type materials. P-type materials typically possess higher operating voltages over n-type materials (redox centers which undergo reduction and become negatively charged) which is clearly advantageous for cathode applications. Additionally, charge compensation within ptype materials is established by anion transport from the electrolyte. The smaller solvation shell of anions aids in providing higher ionic diffusion and should enable higher charge/discharge rates.[26]

Analysis of the cyclic voltammagrams of phenazine and N,N'-diphenylphenazine (1) offers insight into the chemical and electrochemical properties of the molecules. The redox processes of 1 occur about 1500 mV more positive than those of phenazine (Figure 1). This is ideal behavior for redox units in cathodes, as it extends the operating voltage of the battery. The analysis of peak to peak separation ( $\Delta E_{peak}$ ) and the ratio of the anodic peak current to the cathodic peak current ( $i_{p,c}/i_{p,c}$ ) of redox events sheds insight into the chemical and electrochemical reversibility of the redox centers (Table 1 and Table S1). The first redox couple, transitioning from the neutral to a -1 state in phenazine and to a



Figure 1. The neutral and reduced states of phenazine and the neutral and oxidized states of N,N'-diphenylphenazine (1). CV profiles at a glassy carbon electrode of 1 mM solutions of phenazine (blue) and 1 (red) obtained in 0.1 M TBAP in acetonitrile at 50 mV/s.

+1 in 1, display  $\Delta E_{peak}$  near the ideally reversible value (58 mV). For the second redox couple from a ± 1 to ± 2 charge state, while 1 maintains a  $\Delta E_{peak}$  of only 66 mV, the  $\Delta E_{peak}$  of phenazine increases to 216 mV, indicating an electrochemically irreversible redox couple. Additionally, the  $i_{p,a}/i_{p,c}$  of the second redox couple in phenazine decreases at increasing scan rates, again corresponding to electrochemical irreversibility and potentially a coupled chemical reaction (Figure S1). Together, this suggests that materials based around 1, will display much higher operating voltages and significantly more stable cycling in cathodes than phenazine.

Analysis of the voltammetric profiles of phenazine in the presence and absence of trifluoroacetic acid (TFA) (to stabilize the reduced state though binding of a proton), **1**, and N,N'-dimethylphenazine (**2**) at a Pt ultramicroelectrode was used to determine the standard electron transfer rate constants (k<sup>0</sup>) (Figure S3). In each case, the values of k<sup>0</sup> indicated facile and fast charge transfer kinetics (Table 1), and therefore should not be rate limiting even at fast rates.<sup>[28]</sup> This small molecule study ensures that rate performance of the reported materials in battery applications will be limited by either electronic conductivity or ionic diffusion through the material, and not the rate at which the redox storage centers can be oxidized or reduced.

Table 1. Values of peak splitting,  $\Delta E_{peak}$ , and standard electron transfer rate constants, k°, for phenazine and small molecule derivatives.

Material	$\Delta E_{\text{peak1}}$	ΔE <sub>peak2</sub>	k°1[cm/s]	k°2 [cm/s]
	$(0 \rightarrow \pm 1)$	$(\pm 1 \rightarrow \pm 2)$		
Phenazine	58 mV	216 mV	2.6 × 10 <sup>-2</sup>	-
Phenazine	107 mV	65 mV	1 4 x 10 <sup>-2</sup>	1 6 x 10 <sup>-2</sup>
+ 50 mM TFA	107 111	00 111	1.1 × 10	1.0 × 10
N,N'-dimethyl-	96 m\/	59 m\/	0.2 + 10-3	9 E v 10-3
phenazine (2)	00 111 0	30 111	9.3 × 10 °	0.5 X 10 °
N,N'-diphenyl-	65 m)/	66 m)/	1 1 10-2	0.0
phenazine (1)			1.1 × 10-	9.3 × 10°

#### Design and characterization of storage materials

When designing a redox active polymer for electrochemical energy storage (EES), any atoms that do not contribute to faradaic processes should be limited. We hypothesized that the core structure of 1 could be preserved and incorporated into a partially conjugated polymer framework through the crosscoupling of 5,10-dihydrophenazine (3) and dichlorobenzene (4). Following a simple reduction of phenazine with sodium dithionite, the newly freed secondary amines of 5,10-dihydrophenazine provide excellent handles for Buchwald-Hartwig cross-coupling reactions. Cross-coupling 3 with 4 yields poly(phenylene-5,10dihydrophenazine) (poly(Ph-PZ)), an insoluble powder which precipitates from solution (Figure 2a). The ratio of 3 to 4 is given in Table 2, entry 1. It can be seen by comparison of the infrared spectra of poly(Ph-PZ) and 1, that the polymer shares a core structure with 1 (Figure S4). As expected, the cyclic voltammogram of the material, in a lithium metal half-cell, exhibits two one-electron oxidations, similar to the CV profile of 1 (Figure 2b).

Cross-linked networks were synthesized to determine the effect of cross-linking on the cathodes' electrochemical properties. We envisaged that tris(4-bromophenyl) amine (**5**) could be copolymerized to cross-link the material (Table 2, entry 2) in order to improve stability and disrupt ordering.<sup>[5,27,28]</sup> Copolymerization of **3** with **5** results in a fully cross-linked material, poly(triarylamine-5,10-dihydrophenazine) (poly(TAA-PZ)) which exhibited much more resistance to dissolution in electrolyte solution than poly(Ph-PZ). This was determined by UV-Vis spectroscopy of filtered electrolyte solution for one week (Figure

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S5). Since any solubility of the active material will result in a loss of capacity upon cycling, decreasing the solubility of the material is critical to achieving near theoretical capacity and stable cycling performance.

In our previous study of cross-linked poly(phenothiazinedimethylphenylenediamine), we observed that over a certain threshold of cross-linking density, rate performance declined as a result of lowered ionic transport through the material.<sup>[14]</sup> Therefore, two molar ratios of **4** and **5** were examined to determine a crosslinking density that would mitigate dissolution while retaining high ion diffusion (Table 2, entries 3 and 4). The molar ratio in poly(Ph-PZ)-10 lead to a decrease in solubility in the electrolyte solution in comparison to poly(Ph-PZ) and poly(Ph-PZ)-50. It is important to note that the degree of polymerization of the final polymer will also play a significant role in determining the polymer solubility. However, the cross-linked nature of the materials precludes determination of molecular weight by conventional methods.

Table 2. Reagent equivalents used in Buchwald-Hartwig cross-coupling step-growth polymerizations to obtain phenazine-based cathode materials.

Entry	Polymer	(4) (equiv)	(5) (equiv)	(6) (equiv)	
1	Poly(Ph-PZ)	1.0	1.0	0.0	
2	Poly(TAA-PZ)	1.0	0.0	0.67	
3	Poly(Ph-PZ)-10	1.0	0.90	0.067	
4	Poly(Ph-PZ)-50	1.0	0.50	0.33	

The incorporation of cross-linker into the material was ensured by taking advantage of the relative rates of monomer cross-coupling reactions in the step growth polymerization. Due to the faster rate of cross-coupling of 4 with aryl bromides over aryl chlorides, we hypothesized that 6 would be more rapidly incorporated into the polymer chains than 5, ensuring cross-linked copolymers.<sup>[29,30]</sup> When the equivalent of 5 to 6 is low, as in poly(Ph-PZ)-10, we expect that the cross-linker will be fully incorporated within the polymer chains, decreasing the polymers solubility under battery conditions. This is supported by the elemental analysis of poly(Ph-PZ)-10 which revealed that no arylbromide end groups were present. By contrast, elemental polv(Ph-PZ)-50 revealed 0.54 percent bromine analysis of content and 0.67 percent chlorine content. The presence of bromine in poly(Ph-PZ)-50 and the propensity of poly(Ph-PZ) for dissolution, suggest that the copolymer of 3 and 5 exceeded its solubility in toluene and precipitated from the reaction solvent before **4** could be incorporated. This would leave a depleted concentration of **5** remaining in solution, resulting in oligomerization between **3** and **4**, as found in poly(Ph-PZ). Therefore, while poly(Ph-PZ)-10 constitutes a homogenously cross-linked material, it is more likely that poly(Ph-PZ)-50 behaves as a mixture of poly(Ph-PZ) and poly(TAA-PZ). The morphology observed by SEM provides additional support for this hypothesis (Figure S6-8).

The crystallinity of the polymers was investigated by X-ray diffraction (XRD). Diffractograms of the polymers revealed their largely amorphous character (Figure S9). At 20 values between 10°-25°, four small, broad peaks were observed in poly(Ph-PZ) and poly(Ph-PZ)-10, indicating some ordering present in the polymer. As expected, this ordering was lost as the amount of **5** was increased in poly(Ph-PZ)-50 and poly(TAA-PZ). However, no T<sub>m</sub> or T<sub>c</sub> was observed up to 200 °C by differential scanning calorimetry (DSC) in any of the synthesized polymers (Figure S10). Therefore, any ordering observed by XRD is likely due to local interactions between aromatic rings and does not suggest any long range ordering within the materials.

#### Coin cell design and cathode conductivity

For high power applications, fast electron transfer and ion transport kinetics are necessary. To singularize the diffusion limited rate of our materials, we aimed to minimize the rate dependence on electronic transport by making the composite conductivity sufficiently high.<sup>[3]</sup> Cathodes of each polymer were prepared as composites with active material, Super P, CMK-3, and poly(vinylidene difluoride) (PVDF) in a 3:3:3:1 ratio. The partially conjugated  $\pi$  system in these materials is expected to enable fast electron transport through the material<sup>[31-33]</sup> and the high carbon content should provide rapid charge transport through the composite, such that the electronic transport should not be limiting. When not limited electronically, the ability of the materials to transport ions should be rate limiting during charge and discharge.

Potentiostatic electrochemical impedance spectroscopy (PEIS) and cyclic voltammetry were used to measure the cathodes' charge transfer resistance and the ion diffusion coefficients, respectively (Figure S15 and S16). The fits for the charge transfer resistance of each of the plots are shown in Table 3 (additional fitting parameters are presented in Table S2). As expected, all four polymers exhibited low charge transfer

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Figure 3. (a.) Charge-discharge profiles of tenth cycle of poly(Ph-PZ), poly(TAA-PZ), poly(Ph-PZ)-10, and poly(Ph-PZ)-50 at 5 C. (b.) Discharge capacity of poly(Ph-PZ), poly(TAA-PZ), poly(Ph-PZ)-10, and poly(Ph-PZ)-10, and poly(Ph-PZ)-50 at 5 C for 500 cycles.

resistance, enabling fast electron transport. The charge transfer resistance of poly(Ph-PZ), poly(Ph-PZ)-10, and poly(Ph-PZ)-50 never exceeded 80  $\Omega$  throughout charging, indicating fast electron transfer regardless of charge state (Figure S17).

Cyclic voltammograms of each cathode were taken over a range of scan rates. Applying the Randles-Sevcik equation, the diffusion coefficients of the  $PF_6^-$  ions through the electrode were determined. Even at fast scan rates, the response remained diffusion limited, as evidenced by the linear plot of peak current vs. the square root of scan rate. The obtained diffusion coefficients of poly(Ph-PZ) and poly(Ph-PZ)-10 are of the order of  $10^{-8}$  cm<sup>2</sup>/s (Table 3). The faster diffusion of  $PF_6^-$ , observed in poly(Ph-PZ) and poly(Ph-PZ)-10, compared to diffusion through poly(Ph-PZ)-50 and poly(TAA-PZ), is attributed to improved ion transport in the less densely cross-linked materials. For all the polymers presented here, the values for the diffusion coefficient were orders of magnitude higher than those of commercial inorganic oxide cathodes, enabling high rate capabilities while maintaining a high utilization of the active material.<sup>[34-37]</sup>

**Table 3.** Charge transfer resistances and diffusion coefficients obtainedfrom PEIS data at 2.7 V vs. Li/Li<sup>+</sup> and CV data, respectively, for poly(Ph-PZ), poly(TAA-PZ), poly(Ph-PZ)-10, and poly(Ph-PZ)-50.

Polymer	R <sub>ct</sub> (Ω)	D <sub>pk 1</sub> (cm <sup>2</sup> /s)	D <sub>pk 2</sub> (cm <sup>2</sup> /s)
Poly(Ph-PZ)	54.0	1.6 × 10 <sup>-8</sup>	1.4 × 10⁻ <sup>8</sup>
Poly(TAA-PZ)	100.7	4.0 × 10 <sup>-9</sup>	2.5 × 10 <sup>-9</sup>
Poly(Ph-PZ)-10	57.3	1.6 × 10 <sup>-8</sup>	1.5 × 10⁻ <sup>8</sup>
Poly(Ph-PZ)-50	49.1	5.3 × 10 <sup>-9</sup>	3.9 × 10 <sup>-9</sup>

#### Material performance in lithium half-cells

The cathodes were cycled in lithium half-cells between 1.5 and 4.3 V at 5 C (Figure 3a), corresponding to a charge/discharge time of 12 minutes; faster than the US Department of Energy target charging rate. Poly(Ph-PZ)-10 exhibited the highest discharge capacity of 223 mAh g<sup>-1</sup>, while the capacity of poly(Ph-PZ) upon discharge was 209 mAh g<sup>-1</sup>. This improvement in capacity in poly(Ph-PZ)-10, despite its lower theoretical capacity (203 mAh g<sup>-1</sup>), is attributed to the aforementioned decrease in solubility over poly(Ph-PZ). Due to the larger percentage of the inactive cross-linker, poly(Ph-PZ)-50 and poly(TAA-PZ) delivered capacities of 187 mAh g<sup>-1</sup> and 177 mAh g<sup>-1</sup>, respectively.

Since the redox activity of the triaryl amine units in the polymers falls outside the electrochemical stability window (4.5 V), they are not able to contribute any charge storage (Figure S18). Through analysis of the CV of poly(TAA-PZ), each redox peak in the CV could be attributed to oxidations from the embedded phenazine. Since there are two triaryl amine units for every three

phenazine units in poly(TAA-PZ), an integral ratio of 2:3 of the area under the peaks in the CV would be expected if either peak was due to oxidation of the triaryl amine units. However, we observe an approximately 1:1 ratio in the CV's of all of the polymers (Figure S19). In all cases, the experimentally measured capacities were slightly higher than the theoretical capacities of the materials due to the additional capacity contribution from the carbon in the cathode composite (Figure S20).

Continued cycling of poly(Ph-PZ), poly(Ph-PZ)-10, poly(Ph-PZ)-50, and poly(TAA-PZ) at a C-rate of 5, illustrates the prolonged stability of each material (Figure 3b, charge capacities and coulombic efficiencies are shown in Figures S21-S24). All polymers exhibited a modest loss in capacity over the first 50 cycles. Thereafter, they retained at least 92% capacity on the 500<sup>th</sup> cycle. Notably, poly(Ph-PZ)-10 still delivered a capacity of 196 mAh g<sup>-1</sup> on the 500<sup>th</sup> cycle. It is evident that optimizing crosslinking density to minimize dissolution while minimally affecting capacity is an effective strategy to design a high energy cathode material. At an average discharge voltage of 3.45 V, the poly(Ph-PZ)-10 exhibits one of the highest energy densities (approximately 770 Wh/kg of active material) of all polymeric cathode materials reported.

The performance of each polymer under even more demanding discharge rates was further analyzed. Figure 4a plots capacity retention, at various discharge rates, as a percentage of the polymer's initial capacity averaged over the first three cycles at 1 C. When discharge rates exceeded 5 C, charging rates were held constant at a C-rate of 5 to ensure a constant initial charge state, isolating the effect of rate on the discharge capacity. It is evident that all of the materials excel under demanding loads as they maintain the majority of their capacity even when discharged at 60 C. Interestingly, poly(Ph-PZ)-10 had the highest capacity retention at high rates of discharge, followed by poly(Ph-PZ)-50. All four of the polymers recovered over 90% of their capacity when the discharge rate was returned to 1 C.

Due to its high capacity, stability, and superior rate performance, poly(Ph-PZ)-10 was cycled at the extraordinary discharge rate of 120 C (Figure 4b). The material delivered a capacity of 220 mAh g<sup>-1</sup>, corresponding to a power density of over 27 kW kg<sup>-1</sup> when normalized to the mass of the entire cathode composite. With continued cycling, the material stabilized as seen in the improved coulombic efficiency with cycling, and the delivery of 198 mAh g<sup>-1</sup> after 1000 cycles. Further tests were run, probing the performance of poly(Ph-PZ)-10 when charging and discharging at increasing rates (Figure 4c). The charging voltage was increased to 4.5 V to ensure full charge at high C-rates. The material still delivered 180 mAh g<sup>-1</sup> when charged and discharged at 120 C and showed excellent capacity recovery when the charge/discharge rate is returned to 0.5 C. At 120 C, poly(Ph-PZ)-



Figure 4. (a.) Discharge capacity retention of poly(Ph-PZ), poly(Ph-PZ)-10, poly(Ph-PZ)-50, poly(TAA-PZ) when discharged at increasing indicated C-rates. (b.) Cycling performance of poly(Ph-PZ)-10, discharged at 120 C, over 1000 cycles. (c.) Discharge capacities and coulombic efficiencies of poly(Ph-PZ)-10 charged at discharged at the denoted C-rates. (d.) Charge-discharge profile of poly(Ph-PZ)-10 charged and discharged at the indicated C-rates.

10 still retains its two discrete plateaus, indicative of a faradaic charge storage mechanism (Figure 4d). These high rate experiments illustrate the ability of amorphous materials to provide fast ion transport and enable high rates of charge/discharge. By tuning the active mass ratio used in the composite, power and energy density can be optimized for specific applications. The energy density of a cathode composite can be driven higher by increasing the active mass loading. Cells with 60% active material in the composite were tested at varying discharge rates. At low C-rates (0.5 C) poly(Ph-PZ)-10 was able to deliever a capacity of 182 mAh g<sup>-1</sup> (Figure S28). When the cell was discharged at progressively higher C-rates (60 C), poly(Ph-



Figure 5. Cycling performance of poly(Ph-PZ)-10 in a sodium metal half-cell at 0.5 C. Inset: Charge-discharge profile of sodium metal half-cell.

PZ)-10 delivered a capacity of 143 mAh g<sup>-1</sup>. Future work will focus on further understanding ionic transport through amorphous organic materials.

#### Performance in sodium half-cells

P-type cathode materials lend themselves to be used in alternative ion batteries. Since anions are responsible for the charge compensation of the oxidized phenazine units, materials based around this redox active unit are largely unaffected by the metal cations in solution. Therefore, the materials presented here could be used in a range of batteries employing anodes such as sodium, magnesium, and potassium without the performance of the cathode being affected. This effect is demonstrated by analyzing the CV profile of poly(Ph-PZ)-10 in a variety of electrolyte salts, shown in Figure S29. The redox peaks of poly(Ph-PZ)-10 retain their shape and magnitude regardless of the nature of the cation in solution.

We sought to determine the eficacy of a poly(Ph-PZ)-10 cathode in a sodium half cell, as sodium ion batteries are touted as being a future alternative EES system to lithium ion batteries (Figure 5). Coin cells were assembled with a sodium metal anode and a poly(Ph-PZ)-10 composite as the cathode with 1 M NaPF<sub>6</sub> in EC/DEC as the electrolyte. Due to a large resistance in the sodium cell, the coin cell was tested at a relatively low C-rate. Cycling the cell at 0.5 C provided a steady discharge capacity of over 160 mAh g<sup>-1</sup> after 100 cycles, comparable to the capacity obtained in a lithium cell. The large charging capacity in the first cycle and the poor coulombic efficiency are attributed to the incompatibility of carbonate-based electrolytes with sodium metal deposition, leading to an increased resistance in the cell, as

observed by PEIS (Figure S30).<sup>[38,39]</sup> To obtain the same results achieved in the lithium cell, each of the components of the sodium coin cell would require further optimization. Still, these results

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demonstrate the ability of poly(Ph-PZ)-10 to function in alternative ion batteries.

#### Conclusions

The performance metrics of the phenazine-based materials described here, as cathodes, are among the highest reported for organic cathode materials. The careful design of a cross-linked copolymer, poly(Ph-PZ)-10, resulted in improved capacity, stability, and rate performance over the linear poly(Ph-PZ). At an average operating voltage of 3.45 V vs. Li/Li+, poly(Ph-PZ)-10 delivers 223 mAh g<sup>-1</sup> and 220 mAh g<sup>-1</sup> at 5C and 120C, respectively. The addition of the cross-linker was shown to enable a higher active material ratio to be used in the cell while maintaining a high percentage of the material's capacity. The family of materials studied here exhibited excellent ionic transport kinetics that resulted in extraordinary capacity retention at very high C-rates. These materials possess energy densities competitive with current commercial lithium ion batteries and power densities comparable to commercial capacitors, while demonstrating the viability of organic cathodes in EES devices. Specifically, this work demonstrates the impact that fast ionic diffusion through amorphous materials has on rate capability.

#### **Experimental Section**

#### **General Synthetic Procedures**

General information regarding reagents can be found in the Supporting information. N,N'-dimethyl-5,10-dihydrophenazine and N,N'-diphenyl-5,10-dihydrophenazine were synthesized employing previously reported methods.<sup>[40,41]</sup>

#### **Fabrication of Coin-Cells**

Device measurements were conducted in CR 2032 coin cell casings, which were assembled in an argon filled glove box with oxygen levels below 1 ppm. The anode was lithium metal and the working electrode was fabricated from a slurry of 30 wt% active material (~0.6 mg/cm<sup>2</sup>), 30 wt% Super P carbon, 30 wt% CMK-3, and 10 wt% PVDF as the binder in NMP. The high loading cathode was fabricated with 60 wt% active material, 15 wt% Super P carbon, 15 wt% CMK-3, and 10 wt% poly(vinylidene fluoride) (PVDF) as binder. The slurries were spread onto a carbon paper current collector using the doctor blade method with one layer of scotch tape. The coated electrode was dried for 2 h at 60 °C followed by 14 h at 110 °C in a vacuum oven. A polypropylene separator (Celgard 2300) or a glass microfiber filter (GF/A, Whatman) was used as the separator between the two electrodes. The electrolyte solution was 1:1 by volume of EC (ethylene carbonate) to DEC (diethyl carbonate) with 1 M LiPF<sub>6</sub> (Aldrich). In cells with the celgard separator, 60 µL of electrolyte solution were used, while 80 µL were used in the cells with the fiber glass separators. An Arbin BT2000 battery tester was used to perform galvanostatic charge-discharge experiments on the coin cells at 25 ° C.

#### Procedure for cyclic voltammetric experiments

Benchtop cyclic voltammetry experiments were performed in a three-compartment glass cell with medium porosity glass frits separating the compartments. An Ag/Ag<sup>+</sup> reference electrode and a Pt wire counter electrode were used. All 3-mm glassy carbon (GC) electrodes were purchased from CH Instruments and used as working electrodes. Prior to the experiment, electrodes were polished using diamond paste and MetaDi Fluid (Buehler). All cyclic voltammetric measurements were done in

0.1 M TBAP in MeCN unless otherwise specified. The potentials in the CVs were corrected for iR drop using a ferrocene reference at different scan rates.

#### Synthesis of 5,10-dihydrophenazine

Ethanol and DI water were degassed by sparging with nitrogen for 30 min. 400 mL of water and 100 mL of ethanol were added to a 1 L round bottom flask. Phenazine (4.00 g, 22.2 mmol, 1 equiv) and sodium dithionite (46.6 g, 268 mmol, 12 equiv) were added and the solution was magnetically stirred under a nitrogen atmosphere. The reaction was heated to reflux under nitrogen and allowed to proceed for 4 hrs. The reaction was deemed complete when no solid blue particulate remained. The reaction was allowed to cool, quickly filtered, and washed with deoxygenated water, yielding 3.57 g (88 % yield) of a light green powder. The product was dried and stored under vacuum until use.

## General Procedure for Buchwald-Hartwig Cross-coupling Polymerizations

The following method was implemented for the synthesis of poly(Ph-PZ), poly(Ph-PZ)-10, poly(Ph-PZ)-50, and poly(TAA-PZ) (the amount of reagents are detailed for each polymer in the following sections). 5,10-dihydrophenazine, dichlorobenzene, tris(4-bromophenyl)amine, sodium tertbutoxide, RuPhos ligand, and RuPhos Pd G2 precatalyst were charged to a schlenk tube. A nitrogen atmosphere was established and toluene was added. The reaction was stirred at 110 °C for 16 hours. Upon completion of the reaction time, the polymer was suspended in dichloromethane and washed with water 3 times. After filtration, the polymer was dried at 65 °C under vacuum.

#### Synthesis of Poly(Ph-PZ)

The general procedure for Buchwald-Hartwig cross-coupling polymerization was followed using 5,10-dihydrophenazine (273 mg, 1.50 mmol, 1 equiv), 1,4-dichlorobenzene (221 mg, 1.50 mmol, 1 equiv), RuPhos (14 mg, 0.03 mmol, 0.02 equiv), RuPhos Pd G2 precatalyst (23 mg, 0.03 mmol, 0.02 equiv), and NaOtBu (346 mg, 3.6 mmol, 2.4 equiv). The polymer (357 mg) was obtained as a tan powder. IR (ATR, cm<sup>-1</sup>): 3033, 1604, 1503, 1476, 1455, 1329, 1260, 1093, 1061, 1015, 908, 817, 723, 620, 559. Elemental Anal. Found: C, 79.63; H, 4.45; Cl, 2.71.

#### Synthesis of Poly(Ph-PZ)-10

The general procedure for Buchwald-Hartwig cross-coupling polymerization was followed using 5,10-dihydrophenazine (273 mg, 1.50 mmol, 1 equiv), 1,4-dichlorobenzene (198.5 mg, 1.35 mmol, 0.9 equiv), tris(4-bromophenyl)amine (48.2 mg, 0.1 mmol, 0.067 equiv), RuPhos ligand (14 mg, 0.03 mmol, 0.02 equiv), RuPhos Pd G2 precatalyst (23 mg, 0.03 mmol, 0.02 equiv), and NaOtBu (346 mg, 3.6 mmol, 2.4 equiv). The polymer (394 mg) was obtained as a brown powder. IR (ATR, cm<sup>-1</sup>): 3033, 1603, 1502, 1476, 1455, 1329, 1259, 1156, 1093, 1061, 1015, 920, 817, 723, 620, 559. Elemental Anal. Found: C, 80.50; H, 4.71; Cl, 1.19.

#### Synthesis of Poly(Ph-PZ)-50

The general procedure for Buchwald-Hartwig cross-coupling polymerization was followed using 5,10-dihydrophenazine (273 mg, 1.50 mmol, 1 equiv), 1,4-dichlorobenzene (110 mg, 0.75 mmol, 0.5 equiv), tris(4-bromophenyl)amine (241 mg, 0.5 mmol, 0.33 equiv), RuPhos ligand (14 mg, 0.03 mmol, 0.02 equiv), RuPhos Pd G2 precatalyst (23 mg, 0.03 mmol, 0.02 equiv), and NaOtBu (346 mg, 3.6 mmol, 2.4 equiv). The polymer (439 mg) was obtained as a brown powder. IR (ATR, cm<sup>-1</sup>): 2079, 1605, 1499, 1479, 1455, 1333, 1280, 1259, 1156, 1093, 1061, 1015,

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820, 730, 617, 555, Elemental Anal, Found: C, 79,96; H, 4,69; Br, 0.54; Cl, 0.67.

#### Synthesis of Poly(TAA-PZ):

The general procedure for Buchwald-Hartwig cross-coupling polymerization was followed using 5,10-dihydrophenazine (273 mg, 1.50 mmol, 1 equiv), tris(4-bromophenyl)amine (482 mg, 1.0 mmol, 0.67 equiv), RuPhos ligand (14 mg, 0.03 mmol, 0.02 equiv), RuPhos Pd G2 precatalyst (23 mg, 0.03 mmol, 0.02 equiv), and NaOtBu (346 mg, 3.6 mmol, 2.4 equiv). The polymer (414 mg) was obtained as a brown powder. IR (ATR, cm<sup>-1</sup>): 3028, 1606, 1497, 1479, 1456, 1310, 1282, 1256, 1158, 1099, 1060, 1013, 822, 817, 732, 616, 553. Elemental Anal. Found: C, 76.83; H, 4.59; Br, 1.49.

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Keywords: electrochemistry • cross-coupling • nitrogen heterocycle • organic cathode • phenazine

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**Cross-linked Cathodes:** A phenazine based polymer, poly(phenylene-5,10-dihydrophenazine), is cross-linked with tris(4-bromophenyl) amine to form a cross-linked network with improved stability and rate capabilities.

Improved Stabilit Improved Rates Cara N. Gannett, Brian M. Peterson, Luxi Shen, Jeesoo Seok, Brett P. Fors\*, Héctor D. Abruña\*

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Cross-linking Effects of Performance Metrics of Phenazine-Based Polymer Cathodes