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Sodium-Ion Battery

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Polymeric Schiff Bases as Low-Voltage Redox Centers for Sodium-Ion Batteries**

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Abstract: *The redox entity comprising two Schiff base groups attached to a phenyl ring (−N=CH−Ar−HC=N−) is reported to be active for sodium-ion storage (Ar = aromatic group). Electroactive polymeric Schiff bases were produced by reaction between non-conjugated aliphatic or conjugated aromatic diamine block with terephthalaldehyde unit. Crystalline polymeric Schiff bases are able to electrochemically store more than one sodium atom per azomethine group at potentials between 0 and 1.5 V versus Na^+/Na. The redox potential can be tuned through conjugation of the polymeric chain and by electron injection from donor substituents in the aromatic rings. Reversible capacities of up to 350 $mA\,h\,g^{-1}$ are achieved when the carbon mixture is optimized with Ketjen Black. Interestingly, the "reverse" configuration (−CH=N−Ar−N=HC−) is not electrochemically active, though isoelectronic.*

Environmentally clean, safe, and affordable electrochemical energy storage systems are needed to enable the full potentiality of discontinuous renewable energy sources.[1] Research on sodium-ion batteries is advancing fast[2] towards lowering the costs of such grid storage devices because of the high abundance and ubiquitous distribution of sodium. The use of polymers and organic molecules based on renewable sources as electroactive materials in energy storage devices would allow low-cost and green alternatives to metal-based electrodes.[3,4]

To date most organic and polymeric materials that have been used for lithium- or sodium-ion batteries are active at voltages high enough to be used as positive electrodes. These compounds include quinones,[5,6] polyketones with N cycles,[7] and polymers such as polyimides[8] amongst others reviewed in Ref. [4], that exhibited conjugation along its molecular structure. To achieve high-voltage electrode materials, electrochemical reduction reactions leading to stable aromatic, or Hückel units should be involved, that is, quinonic going to aromatic. On the contrary, breakage of a Hückel-stabilized entity results in a low-voltage reduction reaction. This serves as a general principle; however there might be subtle differences and competing effects like enlargement of conjugation, loss of planarity, conformational effects, and the nature of the substituent groups that might be responsible for the rule not being always obeyed.

The list of organic compounds that has shown promising performance as negative electrode (anode) in Li- and Na-ion batteries is limited to few carboxylates,[9] including terephthalates.[10–12] An attractive, still unexplored family of organics with the potential to be used as anode is based on the Schiff-base functionality ($R^1HC=NR^2$). Electrochemical activity can be anticipated from the existence of the C=N double bond. Early polarographic studies on aromatic Schiff bases have evidenced electrochemical behavior at low potential in organic electrolyte.[13] Although, the azomethine group ($R^1R^2C=NR^3$) is more easily reducible than the corresponding carbonyl group of the parent compound,[14] the redox voltage can be tuned just by lengthening of the conjugation chain, formation of intramolecular hydrogen bonds or by introduction of electron donor or acceptor groups in the aromatic rings.[15]

Interestingly, amongst the synthesis methods of Schiff bases, the simple condensation reaction from aldehydes and amines is the preferred as it releases H_2O as a by-product[16] which adds value to the environmental aspects of the material. Crivello et al. have reported on a series of papers a detailed study on the different synthesis methods to produce a wide gallery of monomeric and polymeric Schiff bases.[17] Polymeric Schiff bases have high thermal stability and mechanical strength; however their low solubility limits their processing and application. Choice of the appropriate linker between the azomethine units along the polymer chain allows solubility that will benefit the processability of the polymeric Schiff bases as electrodes.[18,19]

Herein we report on several polymeric Schiff bases as negative electrode material for sodium-ion batteries in organic electrolytes. All polymeric Schiff bases have in common the (−N=CH−Ar−HC=N−) repeat unit, with ten π electrons, thus they are Hückel-stabilized. We explore the differences in the electrochemical properties of these polymers by using aromatic and nonaromatic diamine blocks between the terephthalaldehyde monomer units and by addition of donor substituents on the corresponding anil (conventionally the C_6H_5-N moiety) and benzyl rings.

The synthesized and studied polymeric Schiff bases in this work are shown in Figure 1. They are all based on the terephthalaldehyde unit which contains two aldehyde substituents in *para* position of a phenyl ring. Condensation with aliphatic and aromatic diamines yields P1, P2 and P3, P4, P5, and P6, respectively. Their colors range from light yellow, P2,

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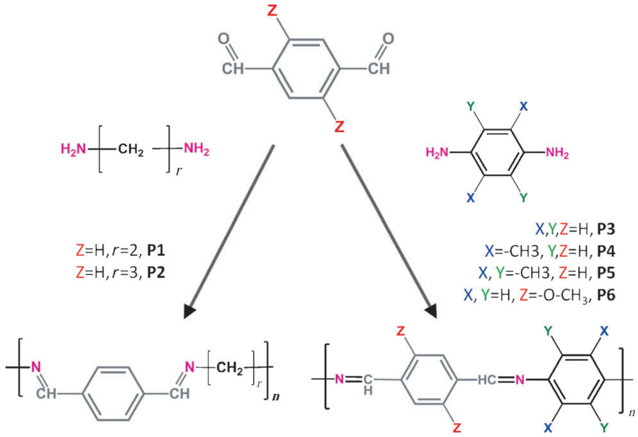

Figure 1. Polymeric Schiff bases obtained by one-step polycondensation reactions of an aromatic dialdehyde, terephthalaldehyde or its derivative, and aliphatic or aromatic diamines. The by-product of the synthetic reaction is H_2O.

to dark orange, P3 or P6 (Table S1). Formation of the azomethine −CH=N−R bond by polycondensation reaction is confirmed by the appearance of the strong imine $\nu_{\mathrm{C=N}}$ stretching band at frequencies 1620–1690 $\mathrm{cm^{-1}}$ (see Figure S1 in the Supporting Information). The stretching frequency of the C=N bond is lowered by conjugation with an additional phenyl ring. (Table S1) The carbonyl $\nu_{\mathrm{C=O}}$ stretching band corresponding to an aldehyde is faintly visible and corresponds probably to end groups. The majority of the synthesized polymeric Schiff bases are crystalline (Figure S1) which is expected to result from π–π interactions between the aromatic rings. Studies concerning the crystal structures will be reported later.

The choice of polymeric Schiff bases with aromatic linkers is made in the search of further conjugation which might improve electrical conductivity and ultimately electrochemical activity. Both, nonconjugated poly-[*N*,*N*′-*p*-(benzylidene)ethylenediamine] (P1) and conjugated poly-[*N*,*N*′-*p*-(benzylidene)-*p*-phenylenediamine] (P3) Schiff bases show electrochemical activity at voltages below 1 Volt versus sodium (Figure 2). The electrolyte has been selected after extensive screening of different solvent–salt mixtures with P3 (Figure S2). Sodium(I) bis(fluorosulfonyl)imide (NaFSI) was selected as ionic salt dissolved in methyltetrahydrofuran (Me-THF) because of the higher capacity values and retention. Capacities of 150 and 180 $\mathrm{mAh\,g^{-1}}$ for P1 and P3, respectively, are achieved at a rate of C/10, being C the current needed to insert two Na^+ ions per monomer in 10 h. Through the first oxidation, 0.9 Na^+ and 1.4 Na^+ ions per monomeric unit are reversibly removed from the polymers P1 and P3, respectively. The additional sodium insertion found in the first reduction is probably due to the electrochemical reaction between sodium and the conductive carbon additive,[20] possibly with electrolyte co-intercalation into the carbon,[21] as well as likely the electrolyte forming a SEI layer from trace water or below the electrochemical voltage stability of the electrolyte.[22] Me-THF is extremely resistant to reduction, but NaFSI has shown some cases of active S−F bonds.[23] Given the reproducible results, we find that the electroactive center in the polymeric Schiff base is −N=CH−Ar−CH=N− which is part of the structure of the monomeric block of the synthesized polymers (P1–P6). However, polymeric Schiff bases containing the inverse unit −CH=N−Ar−N=CH− do not show such electrochemical activity when cycled under the same conditions (Figure S3). This intriguing result is probably due to the nonconjugated −CH=N−Ar−N=CH− unit since the interaction between the two nonbonding electrons on N atoms with sp^2 hybridization and the π electrons of the benzene ring is hindered when the anil ring is coplanar with the rest of the molecule; it is optimal when the ring is at an angle of 90° degrees, where benzylideneaniline is not planar.[24] A loss of conjugation is also suggested by the smallest batochromic shift observed in the C=N stretching of P5 (Figure S1b).

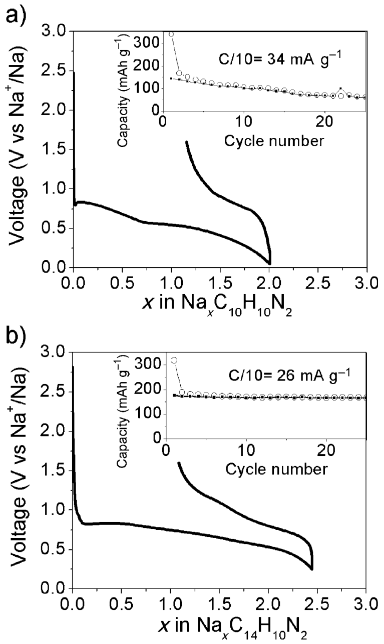

Figure 2. Galvanostatic voltage profile versus the number of sodium ions and electrons inserted during the first reduction and oxidation of a) the nonconjugated polymeric Schiff base P1 and b) the conjugated polymeric Schiff base P3. The insets show the capacity versus cycle number. The cycling conditions are C/10 in 1 M NaFSI/Me-THF electrolyte.

In the case of the electroactive polymeric Schiff bases, despite the aniline ring not being favorably conjugated with the rest of the molecule, the presence of the aromatic linker (Ph) confers a more stable electrochemical activity to P3 than the aliphatic linker (CH_2−CH_2) to P1. This is confirmed for P3, which shows the most stable capacity of about 180 $\mathrm{mAh\,g^{-1}}$ that stays almost constant after 25 cycles while in P1 there is a 60% capacity loss (insets in Figure 2). This reveals that although both polymers are crystalline (Figure S1) the crystallinity being further promoted by the π–π interactions between the benzyl rings, the planarity is more easily kept in the aromatic linked P3.

Examination of PXRD patterns of cycled electrodes of P1 and P3 at the end of the first reduction and at the end of the

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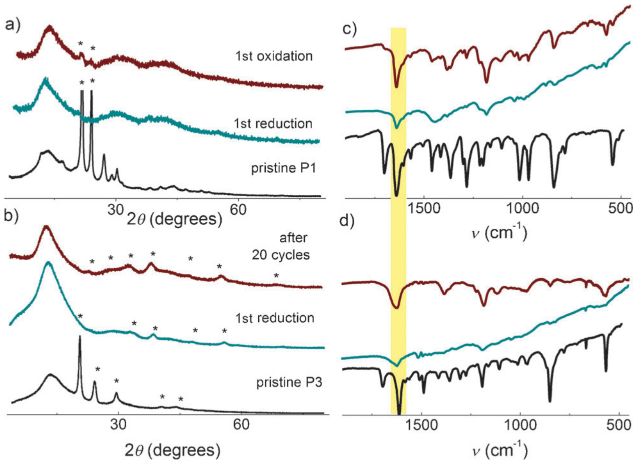

Figure 3. Ex situ PXRD patterns (a,b) and FTIR spectra (c,d) of P1 and P3 comparing the pristine materials (black lines) and the materials after the first reduction (dark cyan lines) and the first oxidation (dark red lines).

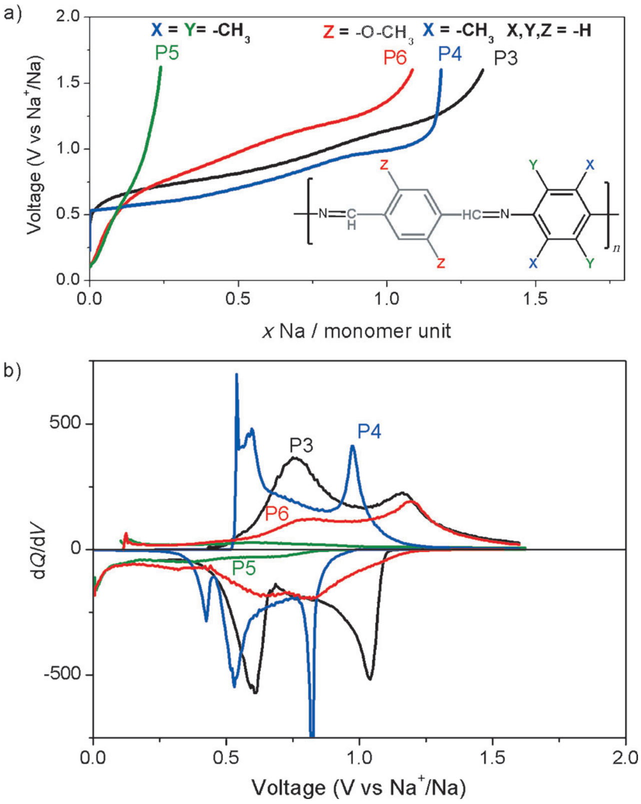

Figure 4. Effect of the electron donor substituents on the redox properties of conjugated polymeric Schiff bases. a) Voltage versus specific capacity for the first galvanostatic oxidation for the polymeric Schiff bases with $X=Y=Z=-H$ (black); with substituents in the aniline ring $X=-CH_3$, $Y=H$ (blue); or $X=Y=-CH_3$ (green); or with substituents in the benzylidene ring $Z=-O-CH_3$ (red). b) Voltage derivatives of the specific capacity versus voltage for the second reduction and oxidation for the same electroactive polymers.

first oxidation shows that the initial quite crystalline structure of the pristine material is lost upon cycling (Figure 3). Nevertheless some small broad reflections remain at the end of reduction process (0.005 V) at different Bragg angles and they are maintained upon oxidation (1.6 V). We think that small crystal domains are being kept during electrochemical cycling providing enough electroactivity to the reaction between the redox-active center and the sodium ions. The loss of crystallinity is purely due to the electrochemical process and/or to polymer swelling by the electrolyte and not to a ball-milling sequence step that was avoided as it tends to increase amorphousness.

FTIR spectra of the same cycled electrodes show that the strong imine vibration band appearing at frequencies of about 1620–1680 cm^{-1}, are maintained upon cyling and therefore there is no breakage of this bond upon sodiation/desodiation, proof of the reversibility of the Na-ion storage process. In general all bands decrease in intensity and resolution in the reduced electrodes.

The electrochemical performance of the polymeric Schiff bases is very promising, showing electrochemical activity versus sodium with low hysteresis, high capacity retention, and stable cycle life. To enhance the energy density of the final battery low-redox-voltage polymeric Schiff bases are desired. To achieve such goal two strategies were followed: 1) changing the number of methyl groups in the linear chain of P1 seeking for an odd/even effect; 2) introducing electron donor substituents in both aromatic rings (two or four methyl groups in the anil or two methoxy groups in the benzyl ring).

First, the addition of a third methylene group in the aliphatic diamine linker, P2, resulted in a major drop of the capacity (Figure S3) rather than lowering the voltage. The result may stem from a decrease in the π stacking with different angles imposed by the 1,3-propylene unit. Regarding the second strategy, the presence of different donor groups attached to either phenyl rings on the monomeric unit of conjugated polymeric Schiff bases had a direct impact on the voltage of reduction and oxidation (Figure 4). An even number of methyl groups were introduced in the anil ring of P3 in respective *para* positions so as to keep its unique conformation yielding poly-[*N*,*N*-*p*-(benzylidene)-*p*-2,5-dimethyl-phenylene-diamine], (P4), and poly-[*N*,*N*-*p*-(benzylidene)-*p*-2,3,5,6-tetramethyl-phenylene-diamine], (P5). Alternatively, two methoxy groups were attached in the benzylidene ring, rendering poly-(*N*,*N*-*p*-(2,5,dimethoxy-benzylidene)-*p*-phenylene-diamine, (P6). For all of them the voltage profile versus the amount of extracted sodium ions during the first galvanostatic oxidation in the voltage range from 0.005 to 1.6 V is shown in Figure 4a.

Substitution with two methyl groups (P4) or two methoxy groups (P6) does not significantly change the amount of sodium that can be inserted in comparison with P3. This translates into minor changes in the capacity and some extra weight because of the introduced substituents. Further addition of two more methyl groups to P4 (P5) leads however to a large capacity drop, which could be due to the loss of planarity and decreased crystallinity (see Figure S1). In addition, this loss of conjugation also would decrease the redox voltage, which under the measured conditions does not seem accessible above 0 V versus Na$^+$/Na. Figure 4a also shows an apparent decrease in the voltage in P4 and an increase in P5 compared to P3, which is quite surprising given that methoxy groups are stronger π donors than the methyl groups. To properly assign the voltage at which a given redox process occurs, the voltage derivative of the capacity versus voltage ($\partial Q/\partial V$) plots are more explicit. The $\partial Q/\partial V$ curves for the second reduction and oxidation, which are reversible processes, are shown in Figure 4b (irreversible first cycle is shown in Figure S4). At a first sight, the results confirm that the voltage is effectively controlled by substitution.

Both reduction and oxidation of parent P3 (Figure 4b) proceed by two different processes at voltages of 0.59 and 1.04 V (reduction) and 0.76 and 1.16 V (oxidation) versus Na^+/Na. The two processes which are 0.4 V apart, may correspond to two one-electron reductions also found 0.2 V apart in molecular benzylideneaniline studied in dimethylformamide (DMF).[25] When two electron-donor methyl groups are introduced on the aniline ring (P4) (Figure 4b, blue line) the voltage shifts down by 0.1–0.2 V. The peaks are centered at 0.53 and 0.82 V for reduction and 0.6 and 0.98 V versus Na^+/Na for oxidation. This results in the lowest voltage anode material that we have synthesized in this work. This low potential along with the lower hysteresis would imply a higher battery voltage. The $\partial Q/\partial V$ plot (Figure 4b) of P6 shows that the addition of two methoxy groups on the benzylidene ring does not really raise the voltage of oxidation for each redox process. However, the amount of charge related to the low-voltage oxidation peak is largely diminished and therefore the average voltage is increased.

From a fundamental viewpoint, to ensure that the maximum sodium insertion and extraction is achieved through proper electronic percolation, and since ball milling is not an option to improve the carbon wiring, large amounts of a high surface area carbon, such as Ketjen Black (KB), is deployed (Figure 5). Optimization of the ratio between KB and carbon super C-65 shows that a mixture with 5 wt% KB and 15 wt% C-65 yields an improved capacity, over 200 mA h g^{-1}, without compromising much the first-cycle irreversible capacity, which is huge when 50 wt% KB is used. Still using 50 wt% KB, which hardly shows any reversible sodium insertion in that voltage range (Figure S5), is interesting because it allows us to achieve the maximum reversible capacity of 350 mA h g^{-1}, which corresponds to 2.8 Na^+ ions per monomer unit or 1.4 Na^+ ions per C=N− moieties in the polymeric chain, which proves that more than one electron is accessible per −C=N− group in agreement with previous studies in organic Schiff base discrete molecule analogs.[25] For the above-mentioned two one-electron mechanism of benzylideneaniline in dimethylformamide (DMF), Martinet et al. proposed that the first electron forms a radical anion in equilibrium between the azo and carbo radical (involving dimerization), and a second electron yields the dianion.[25] Further understanding of the Na-ion storage mechanism in the polymeric Schiff bases is required.

Additional effects on the shift of the maximum redox potential peak by millivolts, as well as a change in the definition and resolution of some redox peaks, narrowing of the first reduction peak and even splitting of the second peak, are observed in the $\partial Q/\partial V$ of the polymeric Schiff bases with different carbon mixtures (Figure S6). This points quite a complex mechanism, the kinetics of which needs to be optimized by proper electrode engineering.

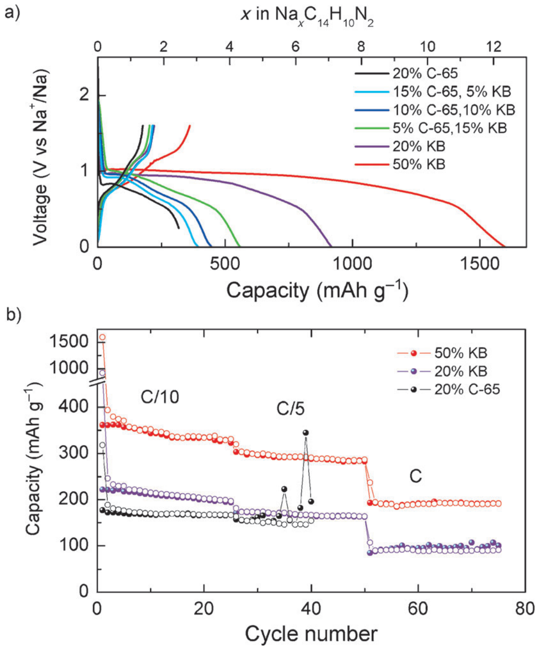

Figure 5. Electrochemical performance of unsubstituted conjugated polymeric Schiff base, P3, with different carbon compositions. a) First cycle voltage versus capacity reduction and oxidation for P3 galvanostatically cycled at a rate of two Na^+ ions/10 h per monomer unit. Large differences in the irreversible capacity found in the first reduction are due to the larger contribution of KB. b) Discharge (empty) and charge (filled) capacities versus cycle number for selected mixtures for different current densities.

The addition of large amounts of carbon also has an impact on the cyclability and C-rate capability of the polymers (Figure 5b). From the reversible 360 mA h g^{-1} achieved in the first cycle at C/10 (26 mA g^{-1}) with 50 wt% KB, 190 mA h g^{-1} are retained after 75 cycles, 25 being of those cycles at 1 C (260 mA g^{-1}). On the other hand when 20 wt% KB is used the initial 220 mA h g^{-1} fall to 90 mA h g^{-1} after 75 cycles following the same protocol. Finally the use of 20 wt% C-65 gives more stable capacities while cycling at C/10 along with better retention at C/5. However at some point during oxidation a long trailing plateau appeared and prolonged cycling at high rates was not possible. The same trailing plateau occurred if P3 + 20 wt% C-65 is reduced below 0.25 V versus Na^+/Na. These results reflect that some carbon C-65-electrolyte interaction must be taking place.

In summary, polymeric Schiff bases, which can be synthesized from aromatic dialdehydes and diamines by simple condensation reaction, are new redox entities active for sodium-ion batteries. The reduction reaction proceeds in two steps in the voltage range from 0.005 to 1.6 V versus Na^+/Na corresponding to two different processes. The redox voltage can be shifted by the addition of the proper substituents in the phenyl rings without compromising the planarity and conjugation. Cycling at rates of 26 mA g^{-1}, capacities of 350 mA h g^{-1} are achieved for unsubsituted poly[*N*,*N*′-*p*(benzylidene)phenylenediamine], which corresponds

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to more than one sodium atom per azomethine C=N− unit. This study has focused on homopolymers, but of course this widens to copolymers of any sort. Processability is one advantage that can be expected, decisive for the electrode manufacture costs, and a possibly optimization of the type and content of the carbon additives. Further, this opens to a new broad and untouched field in the area of low-voltage organic electrodes not only for sodium but also for other chemistries such as lithium- or magnesium-based batteries.

Experimental Section

Synthesis of polymeric Schiff bases: Polymeric Schiff bases were synthesized by polycondensation reaction from diamines (Aldrich: ethylenediamine, 1,3-diaminopropane, *p*-phenylenediamine, 2,3,5,6-tetramethyl-*p*-phenylenediamine and Acros: 2,5-dimethyl-*p*-phenylenediamine) and dialdehydes (Aldrich: terephthalaldehyde and 2,5-dimethoxybenzene-1,4-dicarboxaldehyde) by azeotropic water removal in refluxing toluene as reported by Crivello and co-workers.[17] All reagents were used as received without further purification. Stoichiometric amounts of dialdehyde or diamine were separately dispersed in toluene (Aldrich). After mixing the two dispersions into a round-bottom single-neck flask, the flask was attached to a Dean–Stark apparatus equipped with a reflux condenser and a trap filled with toluene. The mixture was refluxed for 2 h and then the solution was filtered while hot. The collected colored solids were then allowed to dry under vacuum at 80 °C overnight.

Characterization of polymeric Schiff bases: Powder X-ray diffractograms of dried powder samples were collected on a Bruker Advance D8 instrument with copper radiation (CuK$\alpha_{1,2,}$ $\lambda = 1.54056$ Å in the 2θ range from 4 to 80 degrees with a step size of 0.02). Their infrared (IR) spectra were recorded on a PerkinElmer FTIR Spectrum 400 DTGS spectrophotometer in the range of $\nu = 4000–450\ \mathrm{cm}^{-1}$ by preparing KBr pellets.

Electrochemical behavior with sodium: The electrochemical performance versus metallic sodium was measured in CR 2032 coin-type cells. Hand-milled powder mixtures containing 20 % wt Carbon Super C-65 (Timcal) and 80 % wt polymers were directly used as electrode. In some instances a higher surface area carbon, Ketjen Black, or a mixture of Super C-65 and KB were used. Glass fiber Whatman GFB/55 was used as separator and metallic sodium as negative electrode. After testing different electrolyte mixtures 1 M NaFSI (Solvionic) in Me-THF (Aldrich) was selected. Galvanostatic discharge and charge were run in a MACCOR battery tester at current rates of two Na^+ ions/monomeric unit in 10, 5, and 1 h.

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