

Cite this: *Chem. Sci.*, 2022, 13, 9191

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# Investigation of ion-electrode interactions of linear polyimides and alkali metal ions for next generation alternative-ion batteries†

Cara N. Gannett,  ‡ Jaehwan Kim,  ‡ Dave Tirtariyadi,  Phillip J. Milner \* and Héctor D. Abruña\*

Organic electrode materials offer unique opportunities to utilize ion-electrode interactions to develop diverse, versatile, and high-performing secondary batteries, particularly for applications requiring high power densities. However, a lack of well-defined structure–property relationships for redox-active organic materials restricts the advancement of the field. Herein, we investigate a family of diimide-based polymer materials with several charge-compensating ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) in order to systematically probe how redox-active moiety, ion, and polymer flexibility dictate their thermodynamic and kinetic properties. When favorable ion-electrode interactions are employed (e.g., soft  $\text{K}^+$  anions with soft perylenediimide dianions), the resulting batteries demonstrate increased working potentials and improved cycling stabilities. Further, for all polymers examined herein, we demonstrate that  $\text{K}^+$  accesses the highest percentage of redox-active groups due to its small solvation shell/energy. Through crown ether experiments, cyclic voltammetry, and activation energy measurements, we provide insights into the charge compensation mechanisms of three different polymer structures and rationalize these findings in terms of the differing degrees of improvements observed when cycling with  $\text{K}^+$ . Critically, we find that the most flexible polymer enables access to the highest fraction of active sites due to the small activation energy barrier during charge/discharge. These results suggest that improved capacities may be accessible by employing more flexible structures. Overall, our in-depth structure–activity investigation demonstrates how variables such as polymer structure and cation can be used to optimize battery performance and enable the realization of novel battery chemistries.

Received 26th May 2022

Accepted 4th July 2022

DOI: 10.1039/d2sc02939a

rsc.li/chemical-science

## Introduction

As anthropogenic activity increases, the global demand for energy will also continue to grow.<sup>1</sup> Currently, the dominant methods of generating energy (e.g., combustion of fossil fuels) are the leading sources of greenhouse gas emissions.<sup>2,3</sup> Thus, it is imperative that the world quickly transition to renewable energy to avoid irreversible consequences to the planet. However, the intermittent nature of renewable energy sources requires reliable energy storage systems that satisfy the requirements of a sustainable global economy.<sup>4</sup>

Lithium-ion batteries (LIBs) are considered the best-in-class energy-storage technologies due to their high energy densities, long cycle lifetimes, and safety.<sup>5</sup> However, LIBs do not meet all of the requirements of versatile and sustainable energy storage technologies. For example, modern LIBs utilize inorganic cathode materials that are energy-intensive to produce due to the

associated extraction, refinement, and synthesis procedures.<sup>5–8</sup> Moreover,  $\text{Li}^+$  salts also have high extraction and refinement costs, and it is unknown if salt production can match future demand.<sup>9,10</sup> As such, it is desirable to implement alternative ions, such as  $\text{Na}^+$  and  $\text{K}^+$ , into secondary battery technologies.<sup>11,12</sup> However, the rigid and dense structures of modern LIB electrode materials cannot be readily adapted to work with cations other than  $\text{Li}^+$ .<sup>7,8,13–15</sup> Alternative-ion battery research has therefore focused on developing inorganic electrode materials with open framework structures or those involving conversion reactions.<sup>16</sup> Although both approaches show promise, the restrictions of using inorganic cathodes mandates design of a specific electrode material for a specific alternative-ion battery application, limiting their generalizability.

Organic electrode materials have generated increased interest due to their abundant constituents, tunable and flexible structures, and high theoretical specific capacities.<sup>7,8,13–15,17</sup> These qualities make organic electroactive materials sustainable, versatile, and powerful candidates for future battery applications.<sup>18</sup> Further, many organic electrode materials are compatible with a wide range of ions.<sup>19–24</sup> This enables a given material to be studied with different charge-compensating ions in order to systematically investigate how the cation affects

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY, 14850, USA. E-mail: [pjm347@cornell.edu](mailto:pjm347@cornell.edu)

† Electronic supplementary information (ESI) available. See <https://doi.org/10.1039/d2sc02939a>

‡ These authors contributed equally.



battery performance. Recent interest in examining organic electrode materials for alternative-ion batteries has surged, particularly for their use in sodium-ion batteries. However, to date, there are only a handful of studies aimed at systematically understanding how alternative ions perform with a particular material, or family of related materials, in order to elucidate useful structure–property trends that can be generalized to enable future battery development.<sup>13,15,25–30</sup>

Herein, we examine a family of n-type diimide organic electrode materials for their battery performance when paired with different charge-compensating ions (Fig. 1). The common arylene diimide functional group shared by all investigated materials enables us to examine the interactions of ions with redox-active moieties with differing abilities to delocalize electrons within their aromatic structures. We demonstrate that hard-soft acid base theory enables predictions about the interaction strength between cation and reduced polymer, allowing us to predict that, for example, soft  $K^+$  cations perform best when paired with soft perylene diimide (PDI) units. In addition, by investigating several closely related polymers containing PDI units, we reveal that charge compensation mechanism and battery performance are highly dependent on both the polymer structure and the solvation energy of the charge-compensating ions. In contrast to the movement of the field towards rigid crystalline materials such as covalent organic frameworks (COFs),<sup>31</sup> we demonstrate the limiting processes of ion insertion can be minimized in flexible polymers, leading to the highest capacities and rate capabilities reported in this work. These findings point to the importance of systematic studies for uncovering properties of organic electrode materials that can be further optimized for next-generation alternative-ion batteries.

## Results and discussion

### Effect of carbonyl-ion interactions on redox potentials

We set out to understand the role of electrode-ion interactions on the electrochemical performance of battery systems. To

effectively examine these interactions, we varied both the redox-active moiety and the charge-compensating ion in both molecular and polymeric systems. A standardized redox-active functional group, namely, arylene diimide (Fig. 1a), was chosen for this investigation due to the promising performance of arylene diimides as organic electrode materials.<sup>30,32,33</sup> The size of the redox-active unit can be varied by changing the aromatic anhydride used during the synthesis: pyromellitic dianhydride (PMDA) to prepare pyromellitic diimides (PMDIs), 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA) to prepare naphthalene diimides (NDIs), or 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) to produce PDIs (Fig. 1b; see ESI Section 2† for details). Although PDI-based materials are generally considered challenging to prepare due to the poor solubility of PTCDA, we have found that they can generally be synthesized from PTCDA and (poly)amines using molten imidazole as the reaction solvent.<sup>34</sup>

In order to probe the effects of charge-compensating cations on electrochemical performance at the molecular level, **PMDA-di<sup>1</sup>PrAn**, **NTCDA-di<sup>1</sup>PrAn**, and **PTCDA-di<sup>1</sup>PrAn** were synthesized and characterized (Fig. 1c and d). The small molecules were dissolved in *N,N*-dimethylformamide (DMF) and examined by cyclic voltammetry (CV) in the presence of four perchlorate salts:  $LiClO_4$ ,  $NaClO_4$ ,  $KClO_4$ , and  $(tBu_4N)ClO_4$  (TBA<sup>+</sup>). The resulting voltammograms are plotted in Fig. 2a–c. The voltage range was limited to the two-electron reduction of the molecules due to the irreversible decomposition that typically occurs when arylene diimides are further reduced.<sup>28,35–37</sup> As such, two redox couples are observed in each voltammogram, corresponding to reduction to the anion and dianion, respectively.

The potential at which the first redox couple (0/–1) occurs for all three molecules does not significantly vary as a function of the charge-compensating ion. Notably, the formal potential ( $E^{0'}$ ) becomes more positive as the size of the aromatic unit increases ( $E^{0'}(TBA^+)$  for PMDI: –0.736 V → NDI: –0.517 V → PDI: –0.481 V), as the negative charge is more delocalized over the reduced diimide unit (ESI Fig. S88–S90†).<sup>37,38</sup> Additionally,



Fig. 1 (a) Two one-electron reductions of diimides. (b) Tetracarboxylic acid dianhydrides used in this work. (c) Amines used in this work. (d) Synthesis of polymeric diimides.





Fig. 2 Cyclic voltammograms at  $50 \text{ mV s}^{-1}$  of solutions containing (a) PMDA-di<sup>i</sup>PrAn, (b) NTCDA-di<sup>i</sup>PrAn, and (c) PTCDA-di<sup>i</sup>PrAn in DMF in the presence of  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{KClO}_4$ , or TBA<sup>+</sup> (0.1 M). Cyclic voltammograms at  $0.25 \text{ mV s}^{-1}$  of (d) PMDA-pPDA, (e) NTCDA-pPDA, and (f) PTCDA-pPDA in metal (Li, Na, or K) half cells containing 1 : 1 EC : DEC (by vol) in the presence of  $\text{LiPF}_6$ ,  $\text{NaPF}_6$ , or  $\text{KPF}_6$ . The potential scales of the voltammograms were converted to potentials vs. SHE using tabulated values (see ESI† for conversion values).

as the size of the conjugated unit increases, the difference in the potential of the first and second reduction events ( $\Delta E$ ) decreases ( $\Delta E(\text{TBA}^+)$  for PMDI:  $0.786 \text{ V} \rightarrow$  NDI:  $0.553 \text{ V} \rightarrow$  PDI:  $0.288 \text{ V}$ ), resulting in a more stable battery working potential during discharge for the materials with larger aromatic systems. The potential difference arises from electrostatic repulsion; larger conjugated units provide a larger area to delocalize the negative charge and thus ameliorate the destabilizing repulsive effect.<sup>39</sup>

In contrast to the similar potential of the first redox couple across cations, the potential of the second redox couple of PMDA-di<sup>i</sup>PrAn exhibits a strong dependence on the charge-compensating ion (Fig. 2a). As the size of the charge-compensating ion decreases from  $\text{TBA}^+$  to  $\text{Li}^+$ , the redox couple shifts anodically by over 170 mV, which corresponds to a  $16.6 \text{ kJ mol}^{-1}$  increase in the binding energy (ESI Table S13†). A positive shift in the reduction potential with higher charge density ions signals a higher binding energy between the reduced unit and the charge-compensating ion. This behavior is consistent with that of 1,2-diones, for which smaller, more densely charged ions bind more favorably to the reduced carbonyl units.<sup>40</sup> However, this shift is less pronounced for NTCDA-di<sup>i</sup>PrAn and is not observed for PTCDA-di<sup>i</sup>PrAn (ESI Table S13†). This finding suggests that reduced NDI and PDI units are not stabilized to the same extent (or at all) by the interaction with more densely charged ions.

Polymeric materials incorporating arylene diimides were synthesized to investigate if the phenomena observed in solution-state studies extend to battery systems. The diamine *para*-phenylenediamine (pPDA) was reacted with PMDA, NTCDA, and PTCDA to form the linear diimide polymers PMDA-

pPDA, NTCDA-pPDA and PTCDA-pPDA, respectively, by heating the monomers together in imidazole at  $130 \text{ }^\circ\text{C}$  for 24 h. The high quality of the insoluble polymers was confirmed through characterization by  $^1\text{H}$  and cross-polarized (CP)  $^{13}\text{C}$  magic angle spinning (MAS) solid-state nuclear magnetic resonance (SSNMR) spectroscopies, attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy, UV-Vis spectroscopy, powder X-ray diffraction (PXRD), energy dispersive X-ray spectroscopy (EDS), and combustion analysis (see ESI Section 3† for details). In addition, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) confirm the conversion of the monomers into the thermally stable polymers. In particular, all three polymers were confirmed to be free of the corresponding poorly soluble dianhydrides by PXRD, IR, and SSNMR. The successful synthesis of PTCDA-pPDA using this method presents an advantage over previous syntheses of PDI-based polymers that employ Lewis acids such as  $\text{Zn}(\text{OAc})_2$ ,<sup>41,42</sup> as it avoids unnecessary metal waste and minimizes potential decarboxylation of the anhydride units by Lewis acids during the polymerization process.<sup>43</sup>

After synthesis, the polymers were integrated into battery electrodes by mixing 60% active material, 30% Super P carbon, and 10% polyvinylidene fluoride (PVDF) binder by weight. The electrodes were assembled as cathodes into 2032 coin cells using Li, Na, or K metal as the anodes accompanied by the corresponding electrolyte solutions ( $\text{LiPF}_6$ ,  $\text{NaPF}_6$ , or  $\text{KPF}_6$ , respectively) in ethylene carbonate (EC):diethyl carbonate (DEC) (1 : 1 by vol). The EC : DEC mixture was chosen due to its wide electrochemical stability window and broad application in alkali-ion batteries, but a DOL : DME mixture was also







Fig. 3 Cycling performance of (a) PMDA-pPDA, (b) NTCDA-pPDA, and (c) PTCDA-pPDA in metal (Li, Na, K) half cells at a discharge rate of  $100 \text{ mA g}^{-1}$ . Average discharge capacities from rate tests for (d) PMDA-pPDA, (e) NTCDA-pPDA, and (f) PTCDA-pPDA in Li, Na, and K cells. The error bars represent one standard deviation of error in the measured capacity, determined from data obtained from at least three coin cells.

reduced carbonyl units and prevent polymer dissolution. This could explain the more stable cycling performance of **PTCDA-pPDA** with  $\text{K}^+$  and **PMDA-pPDA** with  $\text{Li}^+$ . Material dissolution is a common obstacle for organic electrode materials.<sup>54,55</sup> Utilizing favorable ion-electrode interactions could provide an alternative way to combat this challenge without adding mass or altering the structure of organic electrode materials.

The performances of the three polymers with  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  at different discharge rates were investigated to examine how cation-electrode interactions affect capacity retention at fast discharge rates (Fig. 3d-f, see ESI Fig. S61-S62† for raw data). Among the studied materials, **PTCDA-pPDA** exhibited the best performance in terms of capacity and capacity retention with increasing discharge rate, followed by **NTCDA-pPDA**, and then **PMDA-pPDA**, as predicted previously.<sup>37</sup> This indicates that more of the active sites in **PTCDA-pPDA** are accessible than in **NTCDA-pPDA** and **PMDA-pPDA**, which is likely due to improved electronic access and lowered repulsion between active sites in **PTCDA-pPDA**. Notably, **PTCDA-pPDA** retained 80% of its capacity when its discharge rate was increased from  $0.1 \text{ A g}^{-1}$  to  $10 \text{ A g}^{-1}$  using  $\text{Li}^+$ , while **PMDA-pPDA** retained only 17% of its capacity. Interestingly, the  $\text{K}^+$  cells exhibit the highest capacity at faster rates of discharge in all samples (Fig. 3d-f). For instance, **PTCDA-pPDA** delivered  $56 \text{ mA h g}^{-1}$  in a  $\text{K}^+$  battery and  $50 \text{ mA h g}^{-1}$  in a  $\text{Li}^+$  battery when discharged at  $10 \text{ A g}^{-1}$ , respectively. Thus, the lower solvation energy of  $\text{K}^+$  allows access to more redox-active sites and allows them to be more quickly accessed on the shorter time scales associated with faster charge/discharge rates.<sup>19</sup>

By examining the interactions of PMDI, NDI, and PDI polymers with three different charge-compensating ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,

and  $\text{K}^+$ ), we demonstrate the significant impact of ion-electrode interactions on the thermodynamics and kinetics of the charge/discharge process. The observed trends are consistent with predictions from HSAB theory: by utilizing favorable interactions (hard-hard or soft-soft), the working potential and stability of the battery system increases. Further, for all polymers examined thus far, we observed the highest capacities in  $\text{K}^+$  batteries, demonstrating the promise of pairing  $\text{K}^+$  with organic electrode materials.

### Influence of PDI polymer structure on performance

Having demonstrated the importance of ion-electrode interactions on the thermodynamic properties of battery materials, we sought to better understand their influence on kinetic properties as well. Previous studies have demonstrated that the kinetics of organic battery systems are heavily influenced by the bulk structure of the redox-active material.<sup>56,57</sup> Further, based on our findings above and previous work in the literature, we hypothesized that the kinetics should be influenced by the nature of the solvation shell associated with the charge-compensating ion as well.<sup>19</sup> By varying both the structure of the electroactive materials and the charge-compensating ions, we aim to elucidate how these two parameters interact and ultimately dictate battery performance.

To understand how polymer features such as flexibility and crystallinity influence battery performance, we prepared several polymer materials from the highest performing redox-active moiety, PDI. By altering the structural ordering and chain flexibility of the organic electrode materials, the diffusion of the charge-compensating ions should be significantly altered as well.<sup>56,58,59</sup> In this vein, two additional polymers, **PTCDA-chex**



and **PTCDA-en**, were synthesized from *trans*-1,4-diaminocyclohexane (**chex**) and 1,2-ethylenediamine (**en**) and **PTCDA** to compare with **PTCDA-pPDA** (see ESI Section 3† for details). While **PTCDA-chex** is expected to share the rigidity and tight packing associated with **PTCDA-pPDA**, the non-planar cyclohexane rings should disrupt  $\pi$ - $\pi$  stacking interactions. In contrast, **PTCDA-en** should be both less ordered and more flexible due to the linear alkyl linking units.<sup>58</sup> Indeed, the <sup>1</sup>H SSNMR resonance of the alkyl C-H protons in **PTCDA-en** is sharper than that of **PTCDA-chex**, reflecting their more dynamic and thus liquid-like environment (ESI Fig. S84†). It is worth noting that **PTCDA-chex** and **PTCDA-en** lack extended conjugation between the aromatic units and thus would likely conduct charge *via* charge hopping across PDI units. Preliminary calculations (ESI Fig. S85†) and previous studies on similar aromatic polyimide systems suggest that the optimized structure of **PTCDA-pPDA** is not completely planar either,<sup>60</sup> making delocalization of charge across the fully sp<sup>2</sup>-hybridized polymer unlikely (see ESI Section 6†). Thus, it is expected that the charge transport mechanism is a hybrid of charge hopping across PDI units and limited delocalization of charge through the **pPDA** units in this material.

The PXRD patterns of all three PTCDA-based polymers indicate they are microcrystalline (ESI Fig. S82†). Among the three materials, **PTCDA-pPDA** possesses the greatest number of

sharp reflections by PXRD, including several within the range of  $2\theta = 23$ – $30^\circ$  (corresponding to d-spacings between 3.0–3.8 Å).<sup>61</sup> This suggests that **PTCDA-pPDA** exhibits a higher degree of ordered  $\pi$ - $\pi$  stacking interactions relative to the other two polymers. Consistently, **PTCDA-pPDA** is the only polymer to exhibit significant N<sub>2</sub> uptake at 77 K, with a Brunauer–Emmett–Teller (BET) surface area of 76 m<sup>2</sup> g<sup>-1</sup> (ESI Fig. S78–S79†). In contrast, **PTCDA-en** is only slightly microporous (BET surface area = 10 m<sup>2</sup> g<sup>-1</sup>, ESI Fig. S80–S81†), and **PTCDA-chex** is nonporous to N<sub>2</sub> at 77 K. Rigid polymers often exhibit enhanced surface areas compared to flexible polymers, although these results do not preclude **PTCDA-pPDA** from having densely packed regions that impede ion diffusion.<sup>59,62</sup> Notably, no glass or melting transitions below 300 °C were observed for any of the materials by DSC (ESI Fig. S78†). This indicates that any ordering observed by PXRD likely results from local interactions between the aromatic systems and that the polymers do not possess significant long-range order.

Following the procedure outlined above, **PTCDA-en** and **PTCDA-chex** were assembled into Li, Na, and K half cells and subjected to 100 cycles at a discharge rate of 100 mA g<sup>-1</sup> (Fig. 4a–c). Among the tested combinations, **PTCDA-en** exhibited the highest capacity in the presence of K<sup>+</sup>, delivering an extra 45 mA h g<sup>-1</sup> compared to the Li<sup>+</sup> cell (Fig. 4c). This is greater than the improvement observed with **PTCDA-pPDA**,



Fig. 4 Structural descriptions and cycling performance of (a) **PTCDA-pPDA**, (b) **PTCDA-chex**, and (c) **PTCDA-en** in metal (Li, Na, K) half cells at 100 mA g<sup>-1</sup>. Average discharge capacities from rate tests for (d) **PTCDA-pPDA**, (e) **PTCDA-chex**, and (f) **PTCDA-en** in Li, Na, and K cells. The error bars represent one standard deviation of error in the measured capacity, determined from data obtained from at least three coin cells.









Nathan Lui and Prof. David B. Collum (Cornell University) for assistance with DFT calculations.

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