Dual Anion–Cation Reversible Insertion in a Bipyridinium–Diamide Triad as the Negative Electrode for Aqueous Batteries

Sofia Perticarari, Yuman Sayed-Ahmad-Baraza, Chris Ewels, Philippe Moreau, Dominique Guyomard, Philippe Poizot,* Fabrice Odobel,* and Joël Gaubicher*

Aqueous batteries are an emerging candidate for low-cost and environmentally friendly grid storage systems. Designing such batteries from inexpensive, abundant, recyclable, and nontoxic organic active materials provides a logical step toward improving both the environmental and economic impact of these systems. Herein the first ever battery material that works with simultaneous uptake and release of both cations and anions is proposed by coupling p-type (bipyridinium) and n-type (naphthalene diimide) redox moieties. It represents one of a new family of electrode materials which demonstrates an optimal oxidation potential (−0.47 V vs saturated calomel electrode), extremely fast kinetics, a highly competitive capacity (63 mA h g⁻¹ at 4C), and cyclability in both neutral Na⁺ and Mg²⁺ electrolytes of molar range concentration. Through a combination of UV–vis spectrophotometry, electrochemical quartz-crystal microbalance, Operando synchrotron-X-ray diffraction, and density functional theory calculations a novel dual cation/anion insertion mechanism was proven and rationalized. Based on these findings, this innovative p/n-type product may well provide a viable option for use as a negative electrode material, thereby promoting the design of cutting-edge, low-cost, rocking-chair dual-ion aqueous batteries.

1. Introduction

The increasing importance of clean renewable energy sources, such as sunlight and wind power, being connected to the electrical grid has compounded the necessity for low cost energy storage systems. This fundamental issue hinges on the efficient management and waste minimization of these resources, particularly the storage of surplus power in order to facilitate effective load balancing within the grid.[1] Electrochemical storage of electrical energy constitutes an excellent solution in terms of efficiency and scalability when compared to current alternatives. However, the high cost of installing such battery systems has thwarted its large-scale implementation. Recent advancements have nonetheless demonstrated the possibility of developing sizeable stationary electrochemical storage systems which could fulfill the required cost, durability and power demands.[1] To this end, aqueous electrolytic and ionic batteries constitute a novel and promising technology as they reduce cost (the chief components are cheaper: positive electrode material, separator, electrolyte and cell packaging),[2] risk and environmental impact by comparison to other battery technologies, although this is at the expense of operating potential.[3] Recently there have been an increasing number of publications on sodium-ion aqueous batteries reflecting the advantages of their manufacture, namely lower cost (10 times less) and higher natural abundance of the components (=500 times more) when compared to lithium ones, making them more environmentally sustainable.[1] However, among the vast array of active materials available in the field of Na nonaqueous batteries,[4] very few of them offer the essential combination of adequate potential as well as high chemical and electrochemical stability in aqueous media. The relevant materials and full cells that have demonstrated significant performance in aqueous media are reviewed in Table 1, along with key operational conditions. These results serve to prove that the goal of low cost materials showing sufficient cyclability for cost-effective use can be achieved. However, this approach is associated with relatively low energy density (Table 1), which places even more pressure on the issues of material cost and durability in order to ensure economic viability (≤$100 kWelectric)¹. In this regard, due to partial hydrolysis of cyano ligands in neutral aqueous media,[5] long cycling (>2000 cycles) of the proposed Prussian Blue (PB)...
derivatives (Table 1) has only been demonstrated in either acidic conditions (pH 2)[6] using relatively expensive carbon current collectors, or in a neutral but fairly costly “water-in-salt” electrolyte ([NaClO4] = 10 m) saturated with a Mn(ClO4)2[7] additive. Regarding the PB family, it is however worth noting that recent studies have managed to achieve some enhancements in terms of both capacity and reactivity, thereby permitting the use of a neutral Na2SO4 electrolyte.[8] In the case of the LiMn2O4/Na2SO4 system developed by Whitacre (Table 1, entry 1), they use a less abundant and more costly Li salt to enable the electroactivity of the positive electrode. Moreover, both of these materials require high-temperature synthesis, while the high potential of the positive electrode restricts its depth of charge in thick electrodes[9] in order to avoid excessive O2 release.

We have already underlined the fact that cheap, abundant, green and, most especially, recycle-friendly active materials are crucial constituents of future electrochemical storage systems, and thus that the next logical step would be to substitute transition metal-based materials with organic ones which can be produced from renewable sources and be easily recycled.[10] Furthermore, the continuing concern surrounding the low density of nonaqueous Li batteries with respect to mobile applications becomes much less of an issue when considering stationary electrical storage. Organic materials also offer several distinct advantages over inorganic ones, and these provide significant flexibility as regards the design of aqueous batteries. Firstly, their highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy levels can be very finely and extensively modulated according the donor/acceptor character and the position of substituents, thus allowing for tuning of the redox potential.[11] Secondly, based on the extensive research of Deuchert and Hünig,[12] who reviewed and classified the key redox-active organic systems, three types of ionic batteries can be built: the use of n-type materials (switching from neutral to negative charge state) at both electrodes lead to (i) cationic rocking-chair batteries; similarly, two p-type materials yield (ii) anionic rocking-chair batteries; and (iii) dual-ion batteries, wherein cations and anions both migrate to compensate for the charge arising from the use of p- and n-type materials. Currently, state-of-the-art of aqueous batteries chiefly exploitconfigurations (i) and (ii) (Table 1) In this regard, the only organic materials known to display sufficient cyclability (Table 1, entries 3 and 8) are only suitable for the negative electrode.[14] As an example the polyppyrene-4,5,9,10-tetraone (PPTO) compound developed by Yao and co-workers shows very attractive performance when coupled with LiMn2O4 in neutral Li2SO4 electrolyte.[15] For type (iii) aqueous batteries, only one system has been proposed to date by Nishide and co-workers, which is based on the use of 2,2,6,6-tetramethylpiperidin-1-yl)ox and a conjugated viologen polymer at the positive and negative electrode, respectively.[16] Nearly 1.1 V and 2000 cycles could be reached with good coulombic efficiency using thin film electrodes (∼µm). In the case

<table>
<thead>
<tr>
<th>Materials</th>
<th>Loading</th>
<th>Salt</th>
<th>Q0</th>
<th>(E)</th>
<th>CE</th>
<th>Cycle number</th>
<th>CE</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMO[8]</td>
<td>450</td>
<td>1 m Na2SO4</td>
<td>≈50 (0.005)</td>
<td>+0.7</td>
<td>N/A</td>
<td>Full cell, with ≈30 mg cm−2 electrodes</td>
<td>Full cell, with ≈30 mg cm−2 electrodes</td>
<td>39 (−−) at 0.005 A g−1 with ≈300 mg cm−2 electrodes</td>
</tr>
<tr>
<td>(NTP/AC) [9]</td>
<td>300</td>
<td></td>
<td>≈80 (0.005)</td>
<td>−0.7</td>
<td>300 at 1 mA s−1</td>
<td>2500 (−0)</td>
<td>≈100</td>
<td></td>
</tr>
<tr>
<td>CuHCF[7]</td>
<td>10</td>
<td>10 m NaClO4 sat. Mn(ClO4)2 (buffered at 6.4)</td>
<td>≈50 (0.6)</td>
<td>≈+0.75 (1 A g−1)</td>
<td>Full cell</td>
<td>Full cell</td>
<td>Full cell</td>
<td>27 (−−) at 0.06 A g−1</td>
</tr>
<tr>
<td>MnHCMn[7]</td>
<td>10</td>
<td></td>
<td>≈50 (0.6)</td>
<td>−0.25 (1 A g−1)</td>
<td>50 at 0.6 A g−1</td>
<td>1000 (−0)</td>
<td>99.8 at 0.6 A g−1</td>
<td></td>
</tr>
<tr>
<td>CoCuHCF[7]</td>
<td>2</td>
<td>1 m Na2SO4</td>
<td>40 (1)</td>
<td>≈+0.85 (1 A g−1)</td>
<td>N/A</td>
<td>200 (−−) at 1 A g−1</td>
<td>99.2 at 1 A g−1</td>
<td>27 (−−) at 0.1 A g−1</td>
</tr>
<tr>
<td>SNDI[8]</td>
<td>1</td>
<td></td>
<td>66 (0.5)</td>
<td>≈−0.25 (0.5 A g−1)</td>
<td>250 at 0.5 A g−1</td>
<td>500 (−−) at 0.5 A g−1</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>NaCoHCF[8]</td>
<td>7</td>
<td>1 m Na2SO4</td>
<td>100 (0.65)</td>
<td>≈+0.6</td>
<td>≈10 at 0.13 A g−1</td>
<td>800 (−10) at 0.65 A g−1</td>
<td>≈100 at 0.65 A g−1</td>
<td>N/A</td>
</tr>
<tr>
<td>CuHCF[8]</td>
<td>10</td>
<td>1 m KNO3 (pH12)</td>
<td>≈55 (0.5)</td>
<td>+0.7</td>
<td>50 at 0.5 A g−1</td>
<td>10 000 (−5) at 1 A g−1</td>
<td>99.7 at 1 A g−1</td>
<td>N/A</td>
</tr>
<tr>
<td>NiHCF[8]</td>
<td>7-12</td>
<td>1 m KNO3 or 1 m NaNO3 (pH12)</td>
<td>≈50 (0.5)</td>
<td>≈+0.55 (KNO3)</td>
<td>+0.45 (NaNO3)</td>
<td>500 (−5) at 0.5 A g−1 (KNO3)</td>
<td>99.8 at 0.5 A g−1</td>
<td>N/A</td>
</tr>
<tr>
<td>PEADT[7]</td>
<td>1.5</td>
<td>1 m Zn(BF4)2·6H2O</td>
<td>111 (13.32)</td>
<td>+0.15</td>
<td>N/A</td>
<td>1000 (4) at 13.32</td>
<td>Over 99 at 13.32 A g−1</td>
<td>N/A</td>
</tr>
<tr>
<td>PPTO[7]</td>
<td>2.2</td>
<td>2.5 m Li2SO4 (pH 7)</td>
<td>229 (0.229)</td>
<td>+0.18</td>
<td>N/A</td>
<td>3000 (20) at 0.229</td>
<td>≈100 at 0.229 A g−1</td>
<td>92 (−−) in full cell with LMO at 1C</td>
</tr>
</tbody>
</table>

Table 1. Summary of relevant materials and full cells that have demonstrated significant performance in aqueous media. LMO: LiMn2O4, NTP: C-NaTi2(PO4)3; AC: activated carbon; CuHCF: Copper hexacyano ferrate, MnHCMn: Manganese hexacyanomanganate; NaCoHCF: Na2CoFe(CN)6, SNDI: disodium naphthalene diimide, PPTO: polyppyrene-4,5,9,10-tetraone, PEADT: poly-2,2′-(2-ethynylanthracene-9,10-diylidene)bis(1,3-dithiole); (E) (V): Average potential on discharge/charge for positive/negative materials, respectively. CE (%): coulombic efficiency. Specific energy density values are given per mass of both positive and negative (+−) active materials. ≈: values not explicitly mentioned but approximated from article figures.
of type (iii) ionic batteries, only nonaqueous systems were considered,[17] where the cations (anions) ensure charge neutralization at the negative (positive) electrodes upon charging. Accordingly, the ionic diffusivity in the electrolyte can be greatly weakened, especially if thick electrodes are considered. As mentioned earlier, because low cost is a sine qua non condition with respect to the development of electrochemical systems for grid storage, aqueous batteries need to be built with ultra-thick (>nm) electrodes.[2] These are however plagued by kinetics issues stemming from both the charge and mass transport. For a given porosity and tortuosity, the mass transport within a porous electrode correlates with $L^2/D_0$, where $L$ is its thickness and $D_0$ is the ionic diffusivity within the porosity. Therefore, even for an aqueous electrolyte that shows an ionic diffusivity 20 to 50 times higher than that of conventional Li-ion battery organic electrolytes,[18] the performance of a millimeter thick electrode will still depend on the mass transport. This aspect is nicely illustrated by the presence of opposite pH gradients within both the positive and negative ~2 mm (<100 µm) electrodes on charge[9] (Table 1, entry 1). Such local pH variations are, in addition, potential sources of side reactions with active materials and current collectors, thereby limiting the cycle life and/or imposing the use of costly current collectors. In order to solve these issues, we explore a new type of electrode material that offers the possibility of designing a dual-ion aqueous rocking chair battery where both anions (cations) are reversibly released (inserted) in opposite directions by a single electrode, therefore mitigating mass transport related issues. To achieve this goal both p-type (viologen moiety, referred to as Violo) and n-type (naphthalene diimide moiety, referred to as NDI) moieties have been coupled according to a simple three-step synthesis procedure. The resulting redox-active material enables mixed anion and cation flows at overlapping potentials. All the results point to a very optimistic prognosis with respect to the use of this kind of material in neutral aqueous batteries, by virtue of the synergistic coupling of the two subunits combined at the molecular level.

2. Results and Discussion

In order to create a p/n-type redox material able to exchange both anions and cations within a narrow potential range, we coupled the well-known NDI to bipyridinium units (Violo) through a propyl linker via a simple synthetic procedure summarized in Schema 1. Based on the standard synthesis of perylene–bipyridine derivatives,[19] this new material was prepared in good yield by following a three-step synthesis. Firstly, 1-(3-aminopropyl)-4,4′-bipyridinium bromide hydrobromide (1) was prepared by the nucleophilic substitution reaction between 4,4′-bipyridine and 3-bromopropylamine hydrobromide in acetonitrile, following the customary

![Schema 1. Synthesis of MNV (compound 3).](image-url)
procedure.[20] This compound was obtained in a short reaction time, with a yield of 47%. The second step of the synthesis is an imidization followed by an anion metathesis. Compound 1 was then condensed with 1,4,5,8-naphthalenetetracarboxylic dianhydride, in the presence of imidazole, in 1,2-dichlorobenzene at 80 °C to obtain a red-orange precipitate. The counter-anions were exchanged with perchlorate (ClO₄⁻) to yield compound 2: a yellowish precipitate with a yield of 60%. Finally, dimethylation of the dicaticion salt, compound 2, by treatment with methyl iodide under mild conditions provided the desired compound 3, (referred to as MNV): an orange powder with a yield of 55%. The good solubility of MNV in dimethyl sulfoxide (DMSO) allowed its full characterization by means of ¹H NMR, ¹³C NMR, and HRMS electrospray ionization (ESI) (Figures S1–S5, Supporting Information), while transmission electron microscope (TEM) coupled with energy dispersive X-ray analysis (EDX) confirmed the 1:1 ratio of the two anions I⁻ and ClO₄⁻ (Figures S6 and S7 and Table S1, Supporting Information). Further characterization by Fourier transform infrared spectroscopy (FTIR) and FT-Raman spectroscopy also validated the successful synthesis of the MNV compound (Figures S8 and S9, Supporting Information). Thermal analysis coupled with mass spectrometry revealed that the MNV contains ≈5% water (Figure S10, Supporting Information).

2.1. Electrochemical Performance of MNV

The discovery of a suitable negative electrode material delivering a relatively high capacity, and yet remaining within the potential range slightly above that triggering H₂ evolution, remains the Achilles’ heel of aqueous batteries. Based on the structure of MNV, two sets of electrochemical reactions can be expected (Schema 2): given the initial MNV molecular weight of 1143 g mol⁻¹, a theoretical capacity of 70 mA h g⁻¹ can be reversibly exchanged by MNV upon 3-electron reduction of the two Violo (Violo²⁺) units to a viologen radical (Violo⁺⁺); and the naphthalene diimide core that can be converted from (NDI) to (NDI⁻⁻) radicals. This capacity can, in theory, be doubled with a further 3-electron reduction process of (Violo⁺⁺) and (NDI⁻⁻) to a neutral (Violo) and dianion (NDI²⁻), respectively (Scheme 2). It is worth pointing out however that the neutral viologen structure has been reported to undergo an irreversible redox process.[21]

From the galvanostatic charge–discharge curves at a 4C-rate, shown in Figure 1, MNV displays two overlapping processes with an overall 63 mA h g⁻¹ capacity, 90% of which occurs at a higher potential than the theoretical limit for H₂ production at neutral pH (−0.66 V vs saturated calomel electrode [SCE]). The corresponding average potential on a charge of −0.47 V versus SCE compares favorably with the three other competing materials for the negative electrode of aqueous batteries: (i) it is ≈300 mV lower than that of the hexacyanoferrate (Table 1, entry 2) and diimide derivative (Table 1, entry 3) and, (ii) ≈250 mV higher than that of the Nasicon-type NaTi₂(PO₄)₃[9,22] (Table 1, entry 1), of which the sodiated form leads to H₂ production and local increase of pH.[23] The first third of the MNV capacity occurs through a sharp decrease of the potential followed by a plateau-type profile typical of first-order phase transformation reaction. This is

Schema 2. Overview of the anticipated electrochemistry of MNV in an aqueous electrolyte.
associated with a polarization of \(\approx 130\) mV at a 4C-rate. Interestingly, the remaining capacity corresponds to a sloppy S-shaped process enabling a much lower polarization of less than 40 mV at a 4C-rate. Accordingly, from the chronoamperometric curves shown in Figure S11 in the Supporting Information, one notes the occurrence of both biphasic and diffusion-like currents during the high and low potential region processes, respectively.

Another remarkable advantage of this MNV compound is demonstrated by its ability to sustain high charge–current density, impacting neither the average voltage nor the capacity in any significant way. Both follow a linear dependence along with the increase of current flow, suggesting limitations arising from the electrolyte (inset of Figure 1a). Correspondingly, the internal resistance of this cell is fairly low (8.5 \(\Omega\) cm\(^{-2}\)), which allows for the preservation of a polarization lower than 100 mV at the highest current of 2.4 A g\(^{-1}\), such as was observed for the hexacyanomanganate derivatives cycled with a similar electrode loading (Table 1, entry 2). According to the Prosini model, the linear dependence of the capacity on the current flow enables the determination of the global response time of the electrode \(k\). The latter is \(\approx 4.10^{-3}\) h, which is about 50 to 100 times lower than that observed in typical organic electrolytes. Consequently, 80% of the capacity delivered at 0.3 A g\(^{-1}\) (4C-rate) is retained with a current which is 8 times larger (2.4 A g\(^{-1}\), 32C) (Figure 1a). This excellent rate performance is confirmed by power tests in both Na- and Mg-based electrolytes (Figure 1b): (i) full capacity is reached at 2C and (ii) 93% of it is reached upon a pulse current which is 64 times greater. These results therefore demonstrate that MNV does not limit the high kinetics associated with the aqueous electrolyte. Thus the optimization of the cell design should not only give rise to better kinetics, but also potentially improve the actual surface capacity of the electrode (close to 1 mA h cm\(^{-2}\)) upon decreasing the carbon content and increasing the electrode thickness.
 Nonetheless, these results indicate that a relatively high round-trip energy efficiency can be expected from this negative electrode material, thereby decreasing costly energy losses.

To further illustrate the potential of MNV materials with respect to grid storage application, long cycling experiments were conducted both in Na- and Mg-based neutral electrolytes. It is worth mentioning that the use of smaller anions such as Cl\(^-\), Br\(^-\), NO\(_3\)\(^-\), and BF\(_4\)\(^-\) induces the dissolution of MNV, presumably because, on the one hand, they have a less stabilizing effect on the MNV structure owing to a lower screening effect between the two bipyridinium charges, and on the other hand, they have a higher hydrophilicity. The first 460 cycles of a 12 mg MNV cm\(^{-2}\) hand, they have a higher hydrophilicity. The first 460 cycles

...more generally, short-term power fluctuations of renewable energy sources. Lastly, a concern that is rarely discussed in the literature related to aqueous batteries, deals with their self-discharge properties. In the present case, this aspect carries an even greater significance because the two radicals that are formed on discharge can be oxidized upon reaction with O\(_2\)\([25]\). In this regard, we note that our electrochemical cell was not airtight sealed, and therefore that any oxygen traces in the plastic bag under floating periods of 1 min in the discharged state at −0.75 V versus SCE (highlighted by arrows on Figure 1c), the coulombic efficiency remains in the vicinity of 100% ± 0.5 despite the fact that this cut-off potential is below that of thermodynamic hydrogen evolution (0.66 V vs SCE at pH 7). Concomitantly, the pH, which shows a slight increase of 0.2 units during the first 50 cycles, remains stable for the next 400 cycles. Interestingly, substituting a Mg perchlorate electrolyte for the Na one, while keeping the anion concentration constant, leads to a similar initial capacity, with even a slight improvement in cyclability within the same potential window at 0.3 A g\(^{-1}\) (Figure 1d). As shown in Figure 1c for Na electrolyte, when the cut-off potential is lowered (from −0.75 to −0.85 V versus SCE from cycle 60 to 140, Figure 1d) the capacity increases despite the current being 8 times higher.

To demonstrate the synergistic effect arising from the coupling of NDI and Violo cores, materials composed of one of the MNV’s two redox subunits were investigated in the same cycling conditions. Three tests were considered: the first and the second consisted in evaluating dimethyl naphthalene diimide (referred to as DiMeNDI) and dimethyl viologen perchlorate (referred to as DiMeViolo), while the third explored a macroscopic mixture (blend) of DiMeNDI and DiMeViolo in the same molar ratio as in MNV. Cycling curves reported in Figure S12 in the Supporting Information clearly demonstrate the substantial benefit stemming from the coupling of the two redox units at a molecular level. Indeed although the two materials cycled separately as well as their blend show an initial capacity matching the theoretical prediction, they suffer from pronounced capacity fading. These experiments therefore demonstrate the two subunits of MNV synergistically cooperate during the electrochemical process, leading to the best compromise between specific capacity/cyclability.

Another advantage of the MNV material is the ability to tune its capacity and average potential by optimizing the ratio of cut-off potentials to current density. In order to confirm this theory, the potential window was extended down to −1.2 V versus SCE starting from cycle 461 (Figure 1c). This induces a sharp, 133% increase in capacity up to nearly 90 mAh g\(^{-1}\) at 2.4 A g\(^{-1}\) (32C), which is, to the authors’ knowledge, the highest capacity obtained to date in a Na aqueous electrolyte at such high cycling rates. As depicted in Scheme 2, this increase in capacity stems from the possibility to further reduce the two radicals, Violo\(^{•+}\) and NDI\(^{•+}\), to neutral Violo and dianion NDI\(^{2-}\) moieties, respectively. The corresponding galvanostatic charge–discharge curves before and after the change of cut-off potential shows that the profile of the voltage-capacity curve is pursued at lower potentials (Figure S13, Supporting Information). It is however clear that, owing to H\(_2\) production, slowing the cycling rate down by a factor of two (1.2 A g\(^{-1}\)) leads to a marked increase in both the coulombic efficiency and pH, while the capacity retention is significantly altered (Figure 1c, cycles 570–600).

Although this point requires further investigation, the fact that there is a distinct correlation between the coulombic efficiency and the loss of capacity, which both increase simultaneously when reducing the current flow to 1.2 A g\(^{-1}\), substantiates the potential role of hydrogen evolution in inhibiting ion transfer at the surface of the material. Accordingly, setting the current back to 2.4 A g\(^{-1}\) permits the recovery of a stable capacity retention at nearly 75 mA h g\(^{-1}\) and 100% coulombic efficiency for more than 100 cycles. This result demonstrates that MNV can potentially be used to handle transients and, more generally, short-term power fluctuations of renewable energy sources.

In conclusion, MNV possess a considerable advantage over the other reported materials for aqueous batteries due to the fact that it displays a similar or even better performance with respect to capacity and cyclability, but with relatively less concentrated, neutral, cheap (Na- or Mg-based) and safe electrolytes which opens up great opportunities for its practical application.

2.2. Elucidation of the Redox Behavior

An initial indication of the MNV redox behavior can be gleaned by a comparison of its CV profile with that of the materials composed of one of its two redox subunits: DiMeNDI and DiMeViolo (Figure 2). Upon oxidation, the profile of DiMeNDI is characterized by two peaks (at \(E_{\text{pox}} = −0.51\) and \(E_{\text{pox}} = −0.33\) V) in the Na electrolyte, but only one in the Mg electrolyte (at \(E_{\text{pox}} = −0.22\) V). As regards the MNV, a similar profile is observed upon oxidation, which is present both in Mg and Na electrolytes, suggesting that the broad process centered around −0.5 V is not derived from the NDI subunits of MNV. Accordingly, the potential of DiMeViolo is also in the vicinity of −0.5 V (\(E_{\text{pox}} = −0.52\) V) (Figure 2). This leads us to conclude that the highest potential process at \(E_{\text{pox}} > −0.4\) V, which is detected for both DiMeNDI and MNV materials in Na and Mg electrolytes, can be ascribed to the activity of the NDI core.
In order to gain a more accurate insight into the electrochemical behavior of MNV, it was characterized by UV–vis spectroelectrochemistry. An overview of the spectral changes observed during discharge–charge of the MNV electrode is illustrated by the differential spectra reported in Figure S14 in the Supporting Information. The latter reveals that the discharge to −0.75 V versus SCE induces the simultaneous emergence of broad bands centered around 425–500 nm and 760 nm and anionic (NDI•−) (440 nm) radicals at the expense of the initial NDI units (360 and 380 nm), all of which demonstrates a mixed p–n type behavior. The charge returns to a state close to the initial one, although lingering (Violo•+) and (NDI•+) units are still present as reflected by the pale yellowish-green surface in the visible spectral region from scans 38 to 40 (Figure 3a). These remaining radicals match the irreversible capacity (20%, Figure S14, Supporting Information), and can presumably be ascribed to detachment of MNV grains from the FTO collector. In order to set apart the two redox processes occurring on charge, the potential was maintained in between the two redox processes at −0.36 V during a subsequent oxidation (scans 50 to 55, Figure 3b and Figure S14, Supporting Information). Taking into account the overlapping of the two (Violo•*) and (NDI•*) bands in the 425–500 nm region, scans 50 to 52 are associated with a preferential decrease of the broad band centered around 550–600 nm (Violo•*), while that of (NDI•*) remains largely unchanged (Figure 3b). Moreover the last oxidation process is characterized by an isosbestic point (Figure S15, Supporting Information) which indicates that the stoichiometry of the reaction from NDI•− to NDI does not change and that no secondary reaction occurs during the experiment. Consistently, the S-shaped electrochemical process of MNV (Figure 1a) is ascribed to the redox activity of the Violo subunits. This result was corroborated by electrochemical quartz-crystal microbalance (EQCM) measurements, which show that the mass variation occurring during this process matches with the exchange of one ClO4− anion solvated by close to 4 (3.6) water molecules per electron (Figure S16, Supporting Information). However, during the plateau-type process (scans 53 to 55), the bands associated with both p- and n-type radicals decrease simultaneously while those of the initial NDI core in the 350–400 region reappear. Unfortunately, in the high voltage part, EQCM measurements with an AT type quartz systematically resulted in frequency changes of more than one order of magnitude larger than those expected for any plausible combinations of ions and their solvation shell.

We therefore attempted to differentiate between the structural behavior of MNV on cycling with two electrolytes containing the same anion but different cations (NaClO4 2.5 m and Mg(ClO4)2 1.25 m). The plateau-type process being extremely fast, this investigation was conducted by operando X-ray diffraction (XRD) using synchrotron source, which allowed the collection of one diagram every 166 s. The structural evolution during the first cycle in both electrolytes is shown in Figure 4, whereas the corresponding chronoamperometric responses are reported in Figure S17 in the Supporting Information. During the initial stages of the discharge process, so up to the fifth scan, no significant changes was observed, which is in agreement with the low capacity dq/Qmax = 15%.

From scan 6 however, the intensity of the diffraction peaks immediately decreases without any detectable angular shift. This indicates the occurrence of a first-order phase transformation (despite the fact that the chronoamperometric response was still diffusion-like). Concomitantly, a new set of peaks grows at a constant angular shift on scan 11 in NaClO4 and on 13 in Mg(ClO4)2. Interestingly, this sudden emergence of the new phase appears exactly when the chronoamperometric transients show a sharp increase and a distortion away from a Cottrell diffusion-like shape (Figure S17, Supporting Information), indicating that the kinetics of this two-phase process is controlled by the diffusion of the phase boundary. The reverse mechanism is observed on charge in scans 20 and 18 for the Na and Mg electrolytes, respectively. In summary, the two electrolytes display fairly similar behavior. However, while this analysis could be pursued further, the results clearly show that the metric of the new phase depends on the electrolyte, which serves to highlight the key role of the cation (and its solvation sphere) and exposes the dual-ion process associated with this new type of insertion compound.

Given the mixed potential character of the p/n-type reduction mechanism observed for MNV from UV–vis spectroelectrochemistry, spin-polarized density functional theory (DFT) calculations were performed in order get a more accurate understanding of the electron density distribution during the sequential injection of the first three electrons. As a first approximation in this work, the initial molecule was considered without its four counter-aniions, and instead with an infinite delocalized space charge. As expected, structural relaxation brings to a minimum of energy associated with the largest distance between the positively charged Violo subunits. This configuration is referred to as “straight” (Figure 5). Summing Mulliken population analysis over all atoms in each subunit allows us to examine the charge distribution. Including the alkyl connecter groups where some positive charge accumulates,
in the initial charge state there is a total charge of +2.15 e on each Violo, as expected. As the electron density is successively incremented, the stable molecular structure will depend on a competing interplay of factors, including: Coulombic repulsion between neighboring Violo and NDI redox centers in the crystal; pi–pi type stacking interactions between Violo–Violo, NDI–NDI and Violo–NDI; and zwitterions-type interactions between Violo and NDI subunits. While these cannot all be explored in a single-molecule image, an indication of their relative importance can be determined by examining two competing spin-polarized calculations: in the first instance, the molecule is left “straight,” whereas in the second, the molecule is distorted via its alkyl linkers to overlap the Violo and NDI groups (referred to as “folded”).

In both cases the molecule is then allowed to freely geometrically optimize into order to minimize the total system energy. Table 2 lists the change in charge distribution over the different moieties of the molecule upon sequential reduction with three electrons. This reveals that the straight configuration clearly favors the reduction of the Violo groups for the first and second electron, the last one being more evenly shared by NDI and Violo. This trend mirrors the tendency of the system to reduce repulsion between the two positive charges of each viologen subunit. A closer examination of the electron density distribution shows that the electrons are indeed mainly localized on the C-ring and CH$_3$ atoms around the pyridinium (Figure 5a).

The folded configuration generates a redistribution of the electron density in a much more “equi-sharing” way over the two Violo and NDI groups. This effect primarily stems from the molecule’s capacity to minimize its energy by zwitterion-type attraction between the remaining positive charge on the Violo, and the negative charge on the NDI. Accordingly, the relative enthalpy of the folded molecular structure compared to the straight one (both fully optimized) shows that the folded structure is the most stable with respect to the second and successive electrons (Figure 5). The charge state change for the most stable configuration upon each electron addition also clearly demonstrates that the molecular folding between the addition of the first and second electron encourages significant additional electron redistribution to the NDI (Table 2 and Figure 5b).

These two models should, in theory, be considered as extremes of the real case where intermolecular interactions (presumably pi-stacking and coulombic) ensure solid state packing. In the present case, the molecules obviously do not have such a degree of freedom, and this presumably makes the entire structure more prone to phase transformation, as observed from XRD. Other parameters, such as counter-ions that “freeze” the scaffold charges, should also be taken into account to achieve a more accurate modeling of the redox properties. Nevertheless, these preliminary calculations show that coulombic interactions, such as those expected.
between molecules in the solid state, play a large role in the electron redistribution on reduction and, more especially, push toward a mixed p–n redox process in agreement with spectroelectrochemistry results.

3. Conclusion

By virtue of a facile, inexpensive and highly scalable synthesis procedure, a water-insoluble bipyridinium–naphthalene diimide mixed p/n-type salt was readily obtained. The synergistic coupling of these two units delivers a pleasing potential and fast kinetics, as well competitive capacity and cyclability in both sodium and magnesium neutral electrolytes within the molar concentration range. Combined UV–vis, EQCM, Operando XRD, and DFT calculations permitted the rationalization of the intriguing redox behavior surrounding this compound: the initial 1/3 of the capacity corresponds to the mixed p/n-type redox behavior of both the bipyridinium and the naphthalene diimide cores, which leads to a dual

Figure 4. Structural evolution of MNV during the first cycle (scans 1 to 33) in a) NaClO$_4$ 2.5 M and b) Mg(ClO$_4$)$_2$ 1.25 M.
cation/anion insertion mechanism. The remaining 2/3 were proven to be associated with the bipyridinium moiety along with the concomitant insertion/deinsertion of solvated anions. Given the structural versatility of such materials, we believe the present findings open up new avenues for designing high-energy-density and low-cost, rocking-chair, dual-ion aqueous batteries destined for use in grid storage systems.

4. Experimental Section

Synthesis Procedures: All reactions were carried out under a nitrogen atmosphere. All commercially obtained solvents and reagents were used without further purification unless noted. The 1,4,5,8-naphthalenetetracarboxylic dianhydride, 4,4′-pyridyldi(1-(3-aminopropyl)pyridinium bromide hydrobromide salt (1) (213 mg, 0.5711 mmol), 4-dimethylaminopyridine (DMAP), 64 mg, 0.5706 mmol), and imidazole (77 mg, 1.13 mmol) in e-dichlorobenzene (5 mL) was heated at 80 °C with stirring for 12 h. After cooling, the resulting precipitate was collected by filtration. The collected red solid was dissolved in water (50 mL) and the solution was then washed with methylene chloride to remove water-insoluble residues. An excess quantity of sodium perchlorate powder was added to the separated water layer. The resulting white precipitates were collected by filtration and dried under vacuum (227 mg, 0.2643 mmol, 63%).

1H NMR (300 MHz, DMSO-d6): δ 9.25 (d, J = 6.8 Hz, 4H), 8.88 (d, J = 6.0 Hz, 4H), 8.73 (s, 4H), 8.65 (d, J = 6.8 Hz, 4H), 8.04 (d, J = 5.8 Hz, 4H), 4.77 (t, J = 7.6 Hz, 4H), 4.22 (t, 4H); FTIR/ATR (cm−1): 3036, 1701 (C=N imide asym.), 1659 (C=N imide sym.), 1536 (C=N sym.), 1505, 1450, 1375, 1333, 1244, 1179, 1082 (ClO4−), 816, 765, 620.

Compound 3: A mixture of compound 2 (173 mg, 0.20143 mmol) and iodomethane (503 μL) in acetonitrile (63 mL) was refluxed at 90 °C for 24 h. After cooling to room temperature, the resulting precipitate was collected by filtration, washed with acetonitrile, and finally dried under vacuum (120 mg, 0.1050 mmol, 52%).

1H NMR (300 MHz, DMSO-d6): δ 9.40 (d, J = 6.7 Hz, 4H), 9.28 (d, J = 8.5 Hz, 4H), 8.84 (d, J = 8.6 Hz, 4H), 8.77 (d, J = 4.4 Hz, 4H), 8.76 (s, 4H), 4.83 (t, 4H), 4.45 (s, 6H), 4.25 (t, 4H); 13C NMR (125 MHz, DMSO-d6): δ 163.54, 149.41, 148.64, 147.10, 146.35, 131.00, 126.94, 126.74, 126.47, 126.10, 132.66, 129.46, 119.56, 117.90, 108.50, 108.10, 107.90, 102.30; HRMS (ESI) m/z calculated for C25H17N2O2Cl2: 410.0659 (M+1)+, found 410.0545; FTIR/ATR (cm−1):3033, 1706 (C=N imide asym.), 1659 (C=N imide sym.), 1640 (C=N sym.), 1505, 1450, 1375, 1333, 1244, 1174, 1086 (ClO4−), 816, 765, 620; energy-dispersive X-ray spectroscopy (EDS) (%): calc for C25H17N2O2Cl2: C 47.58, H 3.32, N 5.68, O 19.75, Cl 15.53; found for C25H17N2O2Cl2: C 47.60, H 3.38, N 5.53, O 19.71, Cl 15.44; Anal. calc. for C25H17N2O2Cl2: H 0.70. 3DFT Method: Spin-unrestricted density functional calculations were performed using the AIMP40 code[26–28] with the LDA-PW92 exchange-correlation functional. Periodic boundary conditions were applied (ae0 = 80 au), and energies converged to <10−7 Ha. Electronic levels were filled using a Fermi occupation function to aid convergence, with kT = 0.04 eV. Charge density was fitted using plane-waves with an energy cut-off of 220 Ha. Relativistic pseudopotentials, generated using the Hartwigsen–Goedecker–Hutter scheme,[10] were expanded via Gaussian-based polynomials up to l = 2, with 38/40/40/12 independent Gaussian functions per carbon/nitrogen/oxygen/hydrogen. Atomic charge states were calculated using Mulliken population analysis.

Characterization Techniques: 1H NMR spectra were acquired using a Bruker ARX 300 MHz spectrometer. 13C NMR spectra were recorded on a Bruker 500 MHz, operating at 125 MHz, using a dual 1H/13C cryo probe. Spectra were recorded at room temperature, chemical shifts are written in ppm, and coupling constant in Hz. Multiplicity is presented in the following way: s = singlet, d = doublet, t = triplet, q = quintuplet, m = multiplet. HRMS spectrometry was recorded on a XEVO G2-XS QTOF (Waters) operating on ESI+. The sample was solubilized in DMSO and acetonitrile and the analysis was carried out in acetonitrile. FT-Raman spectra were obtained by means of Jobin-Yvon T64000. Elemental
analyses were performed using a Thermo Scientific Flash 2000 CHNS. Thermal analyses were performed with a NETZSCH STA 449F3 device under Argon atmosphere. FTIR spectra were collected with a Bruker Vertex 70 device in ATR mode, using a DTGS detector at a resolution of 4 cm⁻¹. Scanning electron microscopy was performed using a JEOL JSM-7600F microscope. EDS was performed with a Hitachi HF-2000 TEM, equipped with a field emission gun, operated at 100 kV. Powders were collected on a lacy grid and placed on a High Resolution Transmission Electron Microscope cooling sample holder. All images were acquired at −170 °C (liquid nitrogen).

**Electrochemical Study:** EQCM was performed with a Stanford Research Systems QCM200 Digital Controller and a QCM25 Crystal Oscillator (5 MHz Crystal). UV–vis spectroelectrochemistry was conducted by inserting a home-made, airtight three-electrode quartz cell into a Shimadzu UV-2501 PC spectrometer. Each scan was recorded from 250 to 800 nm within ~1 min. Electrochemical tests were performed using an SP 300 potentiostat from Bio-logic SAS (Clai, France). Compound 3 was characterized by cyclic voltammetry, potentiodynamic and galvanostatic cycling in NaClO₄ 2.5 M and Mg(ClO₄)₂ 1.25 m perchlorate aqueous electrolytes, using a threefold-size counter-electrode (80 wt% activated carbon Norit 1600, 10 wt% Ketjen Black, and 10 wt% polytetrafluoroethylene (PTFE)) to ensure that its potential remained in the 0 to −1 mV region versus the SCE, which was used as the reference electrode. All tests were performed within a glove bag under N₂ flow. Electrolytes were degassed with argon bubbling for 1 h within the glove bag prior to use. Power tests on charge have been carried out using the single charge technique consisting of OCV relaxations until ΔU/t < 1 mV min⁻¹ between each current pulse from I_max to I_min. All experiments were conducted twice in order to ensure reproducibility. Experimental errors related to capacity values were always below 3% using our protocols and set-up.

Unless otherwise specified, the electrode composition is 70 wt% active material, 25 wt% Ketjen Black, 5 wt% PTFE. Caution was taken in preparing MNV electrodes with at least 12 m²/m² cm². The mixture was pressed at 5 tons on a stainless steel (AISI 316L) grid current collector. The pH was continuously monitored using a pH probe (Mettler Toledo, France) placed in the vicinity of the positive electrode (a few mm).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

J.G., P.P., and S.P. are thankful to P. Soudan (IMN, CNRS-University of Nantes) for technical assistance with the design of the operando XRD cell, Y. Pellegrin and E. Blart (CEISAM, University of Nantes) for the fruitful discussions and help with the UV spectrometer, V. Silvestre and B. Charrier (CEISAM, University of Nantes) for help with NMR spectrometers, D. Loquet (CEISAM, University of Nantes) for help with elemental analysis. Y.S.B. and C.E. acknowledge funding the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 642742. All of the mentioned authors have contributed to the present manuscript, and all have approved the final version.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

aqueous batteries, cyclability, dual anion cation insertion mechanism, organic electrode materials, p- and n-type

Received: July 20, 2017
Revised: September 21, 2017
Published online: 21017

学霸图书馆

www.xuebalib.com

本文献由“学霸图书馆-文献云下载”收集自网络，仅供学习交流使用。

学霸图书馆（www.xuebalib.com）是一个“整合众多图书馆数据库资源，提供一站式文献检索和下载服务”的24小时在线不限IP图书馆。

图书馆致力于便利、促进学习与科研，提供最强文献下载服务。

图书馆导航：
图书馆首页 文献云下载 图书馆入口 外文数据库大全 疑难文献辅助工具