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Communication

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Increasing the Gravimetric Energy Density of Organic Based Secondary Battery Cathodes Using Small Radius Cations (Li^+ and Mg^{2+})

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Supporting Information

ABSTRACT: One of the major challenges in electrochemical energy storage (EES) is increasing the gravimetric capacity and energy density of the cathode material. Here we demonstrate how to increase the gravimetric energy density of electrical energy storage devices based on the use of organic materials through exploitation of the strong ionic coupling between a reduced carbonyl functionality and small cations such as lithium (Li^+) and magnesium (Mg^{2+}). Binding of the cation to the reduced carbonyl results in a positive shift of the formal reduction potential of the carbonyl couple. This has the effect of increasing the cell voltage which, in turn, results in an increase in the energy density. We show how this interaction can be used to dramatically increase, by up to a factor of 2, the energy density for a selected case study using 1,2-di(thiophen-2-yl)ethane-1,2-dione (DTED). We have carried out electrochemical and computational studies in order to understand the thermodynamic (positive shift of 250 mV and 1 V in the formal potential for the first and second reductions, respectively, of the carbonyl groups of DTED) and kinetic effects between small radii cations (Li^+ and Mg^{2+}) and the reduced carbonyl functionality of carbonyl-based organic molecules (C-bOMs).

One of the most important challenges for enabling the widespread utilization of renewable energy sources, such as solar and wind, consists in developing high efficiency, low cost, high energy density, safe and environmentally benign electrochemical energy storage (EES) devices.[1−4] Among EES devices, lithium ion batteries (LIBs)[1−4] and magnesium ion batteries (MIBs)[6,7] represent attractive and promising alternatives. Currently, LIBs have the highest energy density among EES devices and have captured the attention and efforts of academic and industrial researchers.[1−4] However, the limited supply of lithium, as well as other factors, have spurred the search for alternatives such as MIBs.[5−7]

Currently, most cathode materials are based on the intercalation of lithium into metal oxide (e.g., $LiCoO_2$) or metal phosphate ($LiFePO_4$) lattices.[1] These can be costly (Co is a strategic metal) and their structural and chemical integrity can be compromised, especially if overcharged.[1] Organic compounds represent an emerging and promising alternative as cathodes for EES applications. These materials are largely composed of carbon, nitrogen, oxygen and sulfur, which are abundant and thus inexpensive.[1−4] They are also amorphous, precluding failure of the material due to structural changes and, in principle, would allow for high C-rate operation since the charge/discharge processes do not involve intercalation.

An attractive family of organic molecules that could potentially be used as cathodes materials are carbonyl-based organic molecules (C-bOMs).[1,3,4,8−15] One example of this family of molecules is quinones. In nonaqueous solvents, quinones can be reversibly reduced in two one-electron steps to the anion radical (eq 1) and dianion, (eq 2), respectively.[16−18] The difference in formal potentials between these two redox processes ($\Delta E^{o'}$) is typically on the order of 500 mV.

$$Q + e^- \Leftrightarrow [Q]^{-\bullet} \tag{1}$$

$$[Q]^{-\bullet} + e^- \Leftrightarrow [Q]^{2-} \tag{2}$$

In aqueous media, however, the process changes to a reversible two-electron, two-proton process (eq 3) at potentials that are dramatically shifted positive, typically by hundreds of millivolts. The positive shift is due to the stabilization of the reduced species by the protonation processes and the shift represents an increase in cell voltage for a device incorporating such a redox process.

$$Q + 2e^- + 2H^+ \Leftrightarrow H_2Q \tag{3}$$

This makes C-bOMs attractive molecules to study for electrical energy storage applications because they show electrochemically and chemically reversible behavior, and their reduced forms display a strong ionic interaction with cations.[19,20]

The strong stabilization effect that cations have toward reduced C-bOMs results in a positive shift of the formal potential for the reduction reaction, which in turn increases the gravimetric energy density of the cathode material. It should be also emphasized that we are changing the formal potential without modifying the molecular structure of the C-bOMs. In addition, a wide range of synthetic variations/modifications can be done on C-bOM structures to predictably modify their electrochemical behavior. For example, they can be designed to maximize their interaction with metal cations of interest (i.e.,

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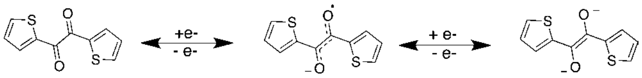
Li^+ and Mg^{2+}),[18−20] and maximize the number of electrons transferred while minimizing the molecular weight of the C-bOMs, thus maximizing the gravimetric energy density.

Energy density represents the delicate interplay of the number of electrons transferred, the voltage at which these process occur and the equivalent mass (per electron transferred). In this communication we demonstrate how to increase the gravimetric energy density of an EES, without changing the electrode material, by exploiting the ionic interaction of the reduced carbonyl moiety and the cation of interest. The molecule DTED is of particular interest because it could be reversibly reduced in two one-electron steps in the presence of noninteracting cations, and, thus, represents a good test case to explore ionic interactions with reduced C-bOM species.

The electrochemical reduction mechanism of 1,2-di-(thiophen-2-yl)ethane-1,2-dione (DTED), which was synthesized using a previously reported method,[14] is presented in Scheme 1. In essence, DTED can be reduced to the radical anion and dianion after one and two electron reduction processes, respectively.

Scheme 1. Electrochemical Reaction Mechanism for DTED



To understand the ionic interactions between the reduced carbonyl moieties and noninteracting cations (tetrabutylammonium-ion (TBA^+), as well as interacting cations lithium-ion (Li^+) and magnesium-ion (Mg^{2+})), we employed rotating disk electrode voltammetry (RDE) and computational methods. To preclude any detrimental effects from water and oxygen, all studies were done in an argon-filled glovebox. A 3-electrode electrochemical cell was used with a glassy carbon (5 mm diameter) working electrode. A high surface area platinum coil was employed as the counter electrode and Ag/Ag^+ served as the reference. For the computational studies, we employed Density Functional Theory[21] (DFT) using B3LYP[22] (using 6-31+G(d,p) basis-set) and the Polarizable Continuum Model[23] (PCM) was used to approximate solvent effects.

The rotating disk voltammograms (RDV) at 65 rpm in different DMF solvent containing perchlorate electrolyte solutions (TBAP, $LiClO_4$ and $Mg(ClO_4)_2$) at 0.1 M concentration are presented in Figure 1. In TBAP, a noninteracting cation which contains tetra-*n*-butylammonium (Figure 1a), two well-defined one-electron processes were observed at −1.36 and −2.20 V (Table 1). However, when small radius cations such as Li^+ and Mg^{2+} were present in the electrolyte, significant changes were evident. In the case of $LiClO_4$ (Figure 1b), a positive shift of 400 mV for the second reduction process was observed. This positive shift reflects the ionic stabilization of the dianion by the Li^+. From the value of the potential shift one can estimate a formation (association) constant of about 6×10^6. A similar, though not as pronounced, effect was observed when Na^+ ions were used (see Figure S1 in Supporting Information). We ascribe this difference in behavior to the differences in ion size and the concomitant differences in ionic interactions. When the same experiment is done using $Mg(ClO_4)_2$, the changes are truly dramatic. When Mg^{2+} is used as the cation, the shift of the second wave is such that rather than observing two one-electron processes (as for TBA^+ and Li^+), a two-electron process was obtained (Figure 1c) at a formal potential of −1.11 V. This represents a positive shift in the formal potential of 0.25 and 1.00 V, for the first and second reduction waves, respectively. This effect is similar to the one observed in the electrochemistry of quinones in aqueous media (vide supra). However, in this case, a nonaqueous solvent was employed.

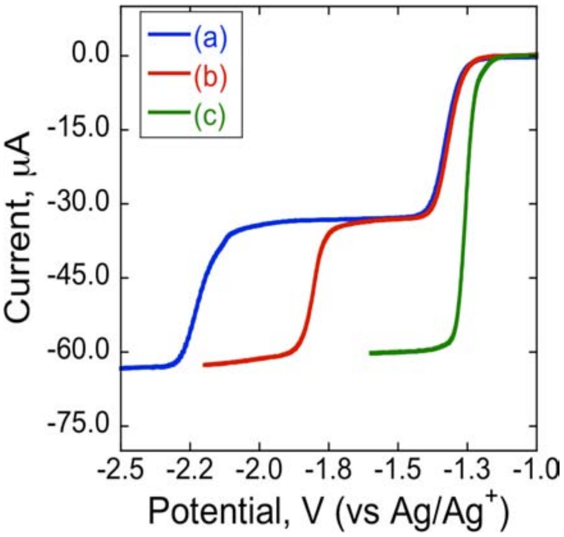


Figure 1. RDVs at 65 rpm for DTED in DMF with (a) TBAP, (b) $LiClO_4$, and (c) $Mg(ClO_4)_2$ electrolyte solutions.

Table 1. Cation effects on the Calculated and Experimental Formal Potentials ($E^{o'}$) for the First and Second Reduction Processes of DTED

	$E^{o'}$, experimental (V vs Ag/Ag^+)		$E^{o'}$, calculated (V vs Ag/Ag^+)	
electrolyte	1st red	2nd red	1st red	2nd red
TBAP	−1.36	−2.20	−1.3	−1.8
$LiClO_4$	−1.35	−1.80	−1.3	−1.6
$Mg(ClO_4)_2$	−1.11		−1.0	−1.1

The consequences of these changes are truly profound. The shift to more positive values means that a battery based on these reactions would exhibit a much higher cell voltage and, thus, energy density. In addition, the fact that for Mg^{2+} the two one-electron waves merge into one two-electron process means that there is no "voltage penalty" as is generally the case for multielectron processes. Moreover, such systems could enable MgIBs which is a system in which the anode material (Mg metal) is 700 mV more positive than Li metal. It should be re-emphasized that the basic chemical reaction, mainly reduction of the carbonyl groups, remains the same. Thus, our stated claim that through the appropriate and judicious choice of cation, one can dramatically enhance the energy density of an organic battery material, as well as enable the use of Mg^{2+} and other multivalent ions (such as Al^{3+} as shown in Figure S1) stands.

To gain a deeper understanding of these processes, we carried out computational studies of the formal potentials of the various species in the presence of TBA^+, Li^+ and Mg^{2+} cations (refer to the Supporting Information to see the validation of the computational method). Table 1 presents the calculated reduction potentials for DTED in the presence of TBA^+, Li^+ and Mg^{2+} cations. As is clear, there is an excellent correspondence with our experimental results. The computa-

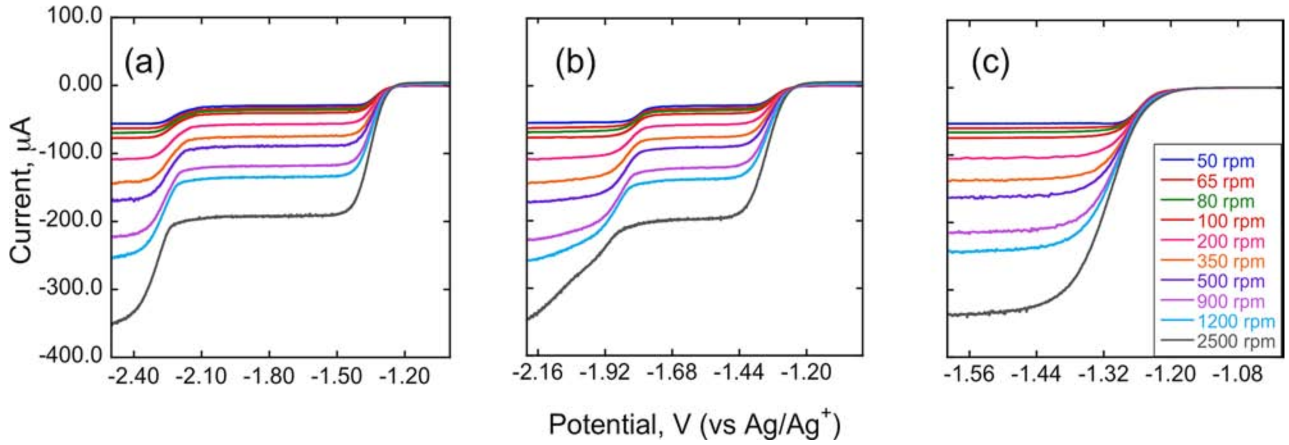


Figure 2. RDVs at different rotating rates for (a) TBAP, (b) $LiClO_4$, and (c) $Mg(ClO_4)$.

tional studies also allowed us to estimate the binding energy of the oxygen atom, from the carbonyl moiety, and the specific cation. In the case of TBA^+, the binding to the reduced carbonyl was small enough to be neglected. Thus, the binding energy was assumed to be 0 eV.[20] On the other hand, the estimated binding energies between lithium-ion and magnesium-ion and the oxygen were −0.9 and −2.0 eV, respectively. The binding energy is a quantitative measure of the ionic coupling between the oxygen in the C-bOMs and the small radius cation. With a higher binding energy (Mg^{2+}), a larger positive shift (thermodynamic stabilization) in the reduction potential is obtained (Figure 1).

RDVs of DTED at different rotation rates in different electrolyte solutions are presented in Figure 2. With these results, it was possible to calculate the heterogeneous charge transfer rate constant (k_f) using the Koutecky−Levich equation (see Supporting Information for the Levich and Koutecky−Levich plots). In these studies, we defined the k_f at specified potentials and, from a knowledge of the magnitude of the computation, we can also calculate the standard rate constant ($k^{o'}$). In these calculations, the transfer coefficient (α) was assumed to be 0.5. The values for k_f and $k^{o'}$ are presented in Table 2. For the first reduction process, the values of $k^{o'}$ were 0.0097, 0.0089, and 0.0022 cm/s for TBA^+, Li^+, and Mg^{2+}, respectively (Table 2). Standard rate constant ($k^{o'}$) values for the second reduction were determined to be 0.0029 and 0.0014 cm/s for TBA^+ and Li^+, respectively. It should be noted that the first redox process in the presence of Mg^{2+} corresponds to a two-electron process. Thus, only one $k^{o'}$ value is reported. From these values, it can be observed that for both TBA^+ and Li^+ the first electron transfer process is faster (3−6 times) than the second. Finally, the standard rate constant value is lower ($TBA^+ > Li^+ > Mg^{2+}$) when the cation has a stronger ionic coupling interaction. Although speculative on our part, we believe that this may be due, at least in part, to electrostatic repulsion effects. However, the electron transfer is thermodynamically favored (potential shift) due to the above-mentioned ionic interaction/stabilization.

Table 2. Cation Effects on k_f and $k^{o'}$ for the First and Second Reduction Processes

cation	k_f, cm/s (potential, V)[a]	$k^{o'}$, cm/s	k_f, cm/s (potential, V)[a]	$k^{o'}$, cm/s
TBA^+	0.041 (−1.41)	0.0097	0.015 (−2.32)	0.0029
Li^+	0.052 (−1.41)	0.0089	0.012 (−1.92)	0.0014
$Mg^{2+,b}$	0.027 (−1.37)	0.0022	n/a	n/a

[a] All the potentials are referenced to Ag/Ag^+. [b] Note that for Mg^{2+} electrolyte the reduction reaction involves 2 electrons.

In summary, we have shown that the energy density of organic based electrical energy storage materials can be dramatically enhanced by ionic interactions. In the present case, we employed a dithiophene dicarbonyl species 1,2-di(thiophen-2-yl)ethane-1,2-dione (DTED) and investigated its redox processes in the presence of noninteracting (TBA^+) as well as strongly interacting (Li^+ and Mg^{2+}) ions. We find that, in the presence of Mg^{2+}, the two one-electron processes presented with a noninteracting cation (TBA^+) are merged into a single two-electron wave and that the formal potential experienced a positive shift greater than 1 V. Computational studies of formal potentials in the presence of TBA^+, Li^+, and Mg^{2+} closely parallel the experimental observations validating our ability to design electrical energy storage materials. We have also studied the charge transfer kinetics and find that the rate of electron transfer decreases with the strength of the ionic interactions ($k^{o'}$, $TBA^+ > Li^+ > Mg^{2+}$). We believe that these observations are of great importance and that they could usher a new generation of organic-based electrical energy storage materials. Further, these studies support the use of Mg^{2+} and possibly other multivalent ions. In fact, preliminary studies (see Supporting Information) indicate that Al^{3+} exhibits analogous behavior with DTED. We are currently pursuing such studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Linear sweep voltammograms for DTED in the presence of the noninteracting cation TBAP, Li^+, Na^+, Mg^{2+}, and Al^{3+}; Levich and Koutecky−Levich plots; validation of the computational method plots; cyclic voltammograms of DTED in the presence of the noninteracting cation TBA^+, Li^+ and Mg^{2+}. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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