Oxygen Redox Versus Oxygen Evolution in Aqueous Electrolytes: Critical Influence of Transition Metals

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Aqueous lithium-ion batteries are promising electrochemical energy storage devices owing to their sustainable nature, low cost, high level of safety, and environmental benignity. The recent development of a high-salt-concentration strategy for aqueous electrolytes, which significantly expands their electrochemical potential window, has created attractive opportunities to explore high-performance electrode materials for aqueous lithium-ion batteries. This study evaluates the compatibility of large-capacity oxygen-redox cathodes with hydrate-melt electrolytes. Using conventional oxygen-redox cathode materials \( \text{Li}_2\text{RuO}_3 \), \( \text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2 \), and \( \text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 \), it is determined that avoiding the use of transition metals with high catalytic activity for the oxygen evolution reaction is the key to ensuring the stable progress of the oxygen redox reaction in concentrated aqueous electrolytes.

1. Introduction

Implementing renewable energy technologies in power grids is imperative for ensuring sustainability. Clean electricity from renewable energy resources can help mitigate climate change and prevent the environmental pollution arising from fossil fuel combustion. However, as renewable energy technologies involve natural processes (e.g., sunlight and wind), their power supply is intrinsically intermittent, and this severely degrades the quality of the electricity supply.[1] Therefore, the load leveling of the intermittent power from renewable energy sources is important.

The use of large-scale electrochemical energy storage devices is an attractive option for ensuring the flexibility of the power grid, which, in turn, would guarantee an efficient and steady power supply. However, lithium-ion batteries, which power most portable electronic devices, are not suitable for this purpose because of their high fabrication/maintenance costs and limited calendar life.[2,3] In particular, flammable organic electrolytes pose an unacceptable fire accident risk while requiring rigorous manufacturing conditions to avoid water contamination.[4] Consequently, lithium-ion batteries based on aqueous electrolytes are an important technical option for large-scale applications, offsetting both the high fabrication/maintenance costs and fire accident risk of their flammable counterparts.[5–7]

Even though significant efforts have been devoted to the development of aqueous lithium-ion batteries for decades, a major obstacle has been their low operational voltage owing to the intrinsically narrow electrochemical potential window of water. The low operational voltage results in a small energy density and severely limits the options available for both positive and negative electrodes. However, a high-salt-concentration strategy developed by Xu et al.[8] and Yamada et al.[9] (involving the use of so-called water-in-salt or hydrate-melt electrolytes) can expand the electrochemical potential window of aqueous electrolytes to more than 3 V. This allows for the use of a greater range of electrodes and should lead to the development of high-performance electrode materials compatible with highly concentrated aqueous electrolytes.[10–17]

In this work, we evaluate the compatibility of lithium-rich transition-metal oxides \( \text{Li}_{1+x}\text{M}_x\text{O}_2 \) (\( \text{M} \): transition metal) with an aqueous electrolyte. A large capacity (>200 mAh g\(^{-1}\)) accumulating both M- and oxygen-redox reactions,[18–20] is essential for increasing the energy density of aqueous batteries. However, the oxygen redox activity possible using highly concentrated aqueous electrolytes has rarely been investigated.[21] Herein, we report the oxygen redox activities of three oxygen-redox positive electrodes \( \text{Li}_2\text{RuO}_3 \), \( \text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2 \), and \( \text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) and elucidate the critical influence of transition metals on oxygen redox activity in aqueous systems.

2. Results and Discussion

\( \text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2 \) and \( \text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) were synthesized by sintering their co-precipitated precursors. \( \text{Li}_2\text{RuO}_3 \) was synthesized by a solid-state method. The X-ray diffraction patterns of all the samples are consistent with those reported previously,[22–25] thus confirming the successful synthesis of the lithium-rich oxides (Figure S1, Supporting Information). These
lithium-rich oxides exhibit capacities greater than 230 mAh g$^{-1}$ in an organic electrolyte (1 m LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) = 1:1 (vol.%)), as is typical for oxygen redox positive electrode materials (Figure S2, Supporting Information).

To evaluate the compatibility of the oxygen-redox electrodes with dilute and concentrated aqueous electrolytes, chronoamperometry was performed using these electrolytes at different potentials in the float mode. The time-dependent anodic-current responses in a 1 m lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) aqueous electrolyte are shown in Figure S3 (Supporting Information). After the application of a constant potential for 4 h, each electrode approaches the steady state and exhibits an anodic leakage current arising from continuous side reactions. Figure 1a shows the steady-state anodic leak current as a function of the applied potential for Li$_2$RuO$_3$, Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$, and Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$. Of the three materials, Li$_2$RuO$_3$ induced an anodic leakage current at the lowest onset potential, which is greater than 1.0 V versus Ag/AgCl (4.14 V vs Li/Li$^{+}$); the anodic leakage current exceeds 20 mA g$^{-1}$ presumably owing to continuous electrolyte oxidation. Although Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ and Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ show slightly higher onset potentials of 1.1 and 1.2 V versus Ag/AgCl, respectively, these potential limits are too low to trigger their oxygen-redox activities. Indeed, charging Li$_2$RuO$_3$ in a 1 m LiTFSI aqueous electrolyte to 0.9 V versus Ag/AgCl results in a small capacity of 119 mAh g$^{-1}$ while causing continuous electrolyte oxidation at voltages greater than 0.9 V versus Ag/AgCl (Figure S4a, Supporting Information). Similarly, neither Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ nor Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ shows a large reversible capacity in the 1 m LiTFSI aqueous electrolyte. Therefore, the oxygen redox activities of these materials cannot be exploited using the 1 m LiTFSI aqueous electrolyte owing to the narrow electrochemical potential window.

On the other hand, a high-salt-concentration strategy can trigger oxygen redox activity. The onset potential of the anodic leakage current of Li$_2$RuO$_3$ is raised to 1.4 V versus Ag/AgCl (4.64 V vs Li/Li$^{+}$) in the hydrate-melt electrolyte Li(TFSI)$_{0.7}$(BETI)$_{0.3}$·2H$_2$O (Figure 1b). Importantly, the suppression of the anodic side reactions aids the activation of oxygen redox reactions, resulting in a capacity as large as ≈300 mAh g$^{-1}$ (Figure S4b, Supporting Information). However, during repeated charge/discharge cycling, the reversible capacity of Li$_2$RuO$_3$ decreases steadily, presumably because of damaging parasitic reactions such as the Li$^{+}$-H$^+$ exchange,[26] or the oxygen evolution reaction (OER).[27]

The onset potential is further up-shifted to 1.7 and 1.8 V versus Ag/AgCl using Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ and Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$, respectively, in a hydrate-melt electrolyte (Figure 1a,b). These voltage limits allow for the realization of a charge capacity of 300 mAh g$^{-1}$ for both electrodes during the first charge (Figure 2a). However, the first discharge capacity of cobalt-containing Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ is 143 mAh g$^{-1}$ with a Coulombic efficiency of 48%, suggesting the simultaneous occurrence of competing anodic side reactions such as electrolyte oxidation.

Figure 1. a) Leakage current values after holding Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ (blue), Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ (red), and Li$_2$RuO$_3$ (black) electrodes at constant potential in Li(TFSI)$_{0.7}$(BETI)$_{0.3}$·2H$_2$O (solid line) and 1 m LiTFSI aqueous solution (dotted line) for 4 h. b) Chronoamperograms of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ (blue), Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ (red), and Li$_2$RuO$_3$ (black) electrodes in Li(TFSI)$_{0.7}$(BETI)$_{0.3}$·2H$_2$O electrolyte.
In contrast, cobalt-free Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ delivers a discharge capacity of 298 mAh g$^{-1}$ at the first discharge with a Coulombic efficiency of ≈100%, which is much higher than that with an organic electrolyte (78%) (Figure S2, Supporting Information). A possible explanation for the additional discharge capacity at the first cycle is the reduction of O$_2$ gas dissolved in the electrolyte, because O$_2$ gas evolution from the cathode surface occurs during the first charge process.[28] Alternatively, or in parallel, as the highly concentrated aqueous electrolytes have the higher electrochemical stability against anodic oxidation than conventional organic electrolytes,[9] parasitic irreversible reactions during the first charge such as electrolyte decomposition and cation densification are suppressed to provide the higher initial Coulombic efficiency. The voltage decay upon cycling is mitigated relative to that for the organic electrolyte (0.06 V decay after 50 cycles for the aqueous electrolyte while 0.11 V decay for the organic electrolyte), because the capacity with the aqueous electrolyte is smaller than that with the organic electrolyte. Importantly, 81% of the initial discharge capacity is retained after 50 charge–discharge cycles (Figure 2b,c), indicating that the operation of the oxygen redox electrode in the concentrated aqueous electrolyte is stable when ruthenium and cobalt are not present in the cathode material.

To confirm the occurrence of the oxygen redox reaction in Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$, ex situ X-ray absorption–emission spectroscopy was conducted during the second cycle (Figure 3a–d). A reversible peak shift is observed in the low-voltage and high-voltage regions for the Mn and Ni K-edges, respectively (Figure 3b,c), highlighting the contributions of both Mn and Ni to the cationic redox capacity. The O K-edge X-ray absorption spectra show that the characteristic absorption at 531 eV emerges/diminishes reversibly during charging/discharging (Figure S5, Supporting Information). Furthermore, the O K-edge resonant inelastic X-ray scattering (RIXS) spectra obtained using an incident photon of 531 eV show a sharp X-ray emission at 523 eV after charging, which is widely recognized as the fingerprint of oxygen oxidation (Figure 3d). All these spectroscopic features are consistent with those reported previously for oxygen redox electrodes in organic electrolytes.[28–32]

An important question to ask here is why only cobalt-free Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ exhibits a reversible oxygen redox capacity in the hydrate-melt system. To determine how cobalt disables the oxygen redox activity, X-ray photoelectron spectroscopy (XPS) was conducted during the first charge in order to evaluate the difference in the surface states. In the case of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$, the peak at a binding energy of 854.5 eV, which is related to the Ni 2p$_{3/2}$ core, blue-shifts to 856 eV after charging to 80 mAh g$^{-1}$ (≈ 1.6 V vs Ag/AgCl). This is followed by the emergence of a new higher-energy shoulder at 857 eV after charging to 300 mAh g$^{-1}$ (≈ 1.8 V vs Ag/AgCl; Figure 4a,b), indicating the continuous oxidation of nickel at the surface. The XPS peak for the Mn 2p$_{3/2}$
core does not change during the first charge because Mn$^{4+}$ in the pristine state cannot be oxidized, confirming reasonable surface oxidation in association with the first charge process.

In striking contrast, when Co-containing Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ is charged to 80 mAh g$^{-1}$, the XPS peak at 854.5 eV, which is related to the Ni 2$p_{3/2}$ core, shifts to 856 eV. However, it returns to 854.5 eV upon further charging to 200 and 300 mAh g$^{-1}$ (Figure 4c,d), indicating Ni undergoes reduction on the particle surfaces owing to the exposure to the large-overpotential environment. It is noteworthy that the voltage plateau at $\approx$1.5 V versus Ag/AgCl, which is characteristic of the initial activation process of the oxygen-redox electrodes, is less obvious than that of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$. Presumably, the oxidized oxide ion in Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ is unstable in aqueous electrolytes to disrupt this activation process.

The reduction of Ni at the surface of Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ is attributable to the high catalytic activity of Co with respect to the oxygen evolution reaction (OER). Layered oxides containing Co, such as CoOOH,$^{[13]}$ Li$_{1-x}$CoO$_2$,,$^{[34,35]}$ and Na$_{0.67}$CoO$_2$,,$^{[36]}$ have been reported to exhibit high OER activity. Consistently, Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ exhibits a slightly larger anodic leakage current in the high-voltage region than that of cobalt-free Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$, as shown in Figure 1b. Presumably, the high OER-activity of cobalt at the surface accelerates the OER, $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$, which is initiated by the primary anodic process of Co$^{3+} + \text{H}_2\text{O} \rightarrow \text{Co}^{4+} \cdot \text{OH} + \text{H}^+$.,$^{[37,38]}$ However, as
the electrochemical potential of the electrons of Ni$^{4+}$ in charged Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ is lower than that of Co$^{3+}$, the spontaneous reduction of Ni occurs as follows: Co$^{4+}$ + Ni$^{4+}$ + H$_2$O → Co$^{3+}$-OH + Ni$^{3+}$ + H$^+$ → Co$^{3+}$-OH + Ni$^{3+}$ + H$^+$ (Scheme 1). This self-discharging process arising from the parasitic side reaction inhibits the oxygen redox activity of Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$. It is also important to note that a Li$_{1.2}$Co$_{0.54}$O$_2$ electrode stably operates with a Co$^{4+/3+}$ redox couple in highly concentrated electrolytes.$^{[19]}$ However, the charged Li$_{1.2}$Ni$_{0.13}$Co$_{0.13}$Mn$_{0.54}$O$_2$ electrode possesses an electronic state consisting of Co$^{3+}$ and oxidized oxide ions such as O$^-$ and/or O$_2$$^-$.$^{[19]}$ As the oxidation of oxide ions causes the M–O bond dissociation, the resulting Co in an under-coordination environment should be highly electrophilic, leading to the self-discharge process in Scheme 1. Therefore, in addition to employing the high-salt-concentration strategy for expanding the electrochemical window, it is also essential to avoid using the...
OER-active transition metals in large-capacity oxygen-redox cathodes in aqueous media. As demonstrated in this study, highly OER-active Ru and Co cannot be considered as the primary options when designing aqueous oxygen-redox batteries.

To further confirm the stable operation of the oxygen redox cathode in the hydrate-melt system, we fabricated a full cell with the Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$|Li(TFSI)$_{0.7}$(BETI)$_{0.3}$·2H$_2$O|Li$_4$Ti$_5$O$_12$ configuration (Figure 5a). After the first activation cycle, the full cell exhibits a specific capacity of 82 Ah per unit weight (kg) of the active materials (224 Ah per unit weight (kg) of the cathode material) at a rate of 0.5 C with an average discharge voltage of 1.75 V and the energy efficiency of 66% (Figure 5b). In other words, it shows an energy density equivalent to or higher than those of the state-of-the-art aqueous lithium-ion batteries (Figure 5d).$^{[8,9,40–43]}$ 81% and 48% of the capacity at 0.5 C rate are retained at the rates of 1 C and 2 C, respectively, supporting the stable operation of the system at high rates (Figure S6, Supporting Information). Notably, 87% of the initial cell capacity is retained after 100 cycles while the average Coulombic efficiency is 97% over 100 cycles (Figure 5c). The full-cell capacity was designed to be limited by the anode capacity (Figure 5a); thus, it is possible to further increase the energy density by balancing the anode/cathode capacities.

3. Conclusion
We demonstrated that additional capacity related to the oxygen redox reaction can be activated in a lithium-rich layered cathode using a highly concentrated aqueous electrolyte. While extending the voltage window using the high-salt-concentration strategy is essential for “activating” the oxygen redox reaction, the suppression of the competitive OER is the key to “stabilizing” the reaction, and ensuring long-term repeated cycling. The presence of highly OER-active transition metals, such as ruthenium and cobalt, significantly accelerates the OER and the subsequent parasitic side reactions, causing rapid degradation. To further demonstrate the stable operation of an aqueous lithium-ion battery that utilizes the extra capacity of the oxygen redox reaction in the cathode material, a full cell with the Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$|Li(TFSI)$_{0.7}$(BETI)$_{0.3}$·2H$_2$O|Li$_4$Ti$_5$O$_12$ configuration was fabricated. The cell showed reasonable long-term stability as well as a record-high energy density. This work
4. Experimental Section

Li1.2Ni0.2Mn0.6O2 and Li1.2Ni0.13Co0.13Mn0.54O2 were synthesized via a co-precipitation method. Nickel sulfate hexahydrate (NiSO4·6H2O), manganese sulfate pentahydrate (MnSO4·5H2O), cobalt sulfate heptahydrate (CoSO4·7H2O), and sodium carbonate (Na2CO3) were used as the starting materials to prepare the Ni1xCo1-xMn3O4 precursors. The precursors were thoroughly mixed with Li2CO3 (5% excess Li) by ball milling and then calcined at 900 °C for 12 h after being pre-sintered at 500 °C for 6 h. Li2RuO3 was synthesized using a solid-state method. Stoichiometric amounts of RuO2 and Li2CO3 (10% excess, to compensate for its volatilization at high temperatures) were thoroughly mixed by ball milling and then calcined at 1000 °C for 24 h.

LiTFSI (Li[SO2CF2]2) and LiBF4 (Li[SO2CF2]2) were purchased from Kishida Chemical. The electrolyte solutions were made using 1,2-dimethoxyethane as solvent; the active material/AB/PVDF weight ratios used were 65/30/5.

The active material powder films (of Li1.2Ni0.2Mn0.6O2 and Li4Ti5O12), the active material powder that used for the positive electrodes (Li1.2Ni0.2Mn0.6O2, Li1.2Ni0.13Co0.13Mn0.54O2) was washed thrice with 1,2-dimethoxyethane to minimize the amount of residual Li salts. The washed electrode was then dried and transferred to the XPS chamber without exposure to air.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aqueous batteries, aqueous electrolyte, batteries, cathodes, oxygen evolution, oxygen redox
