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Revisiting the role of Al^{3+}-based aqueous electrolytes in the charge storage mechanism of MnO_x cathodes

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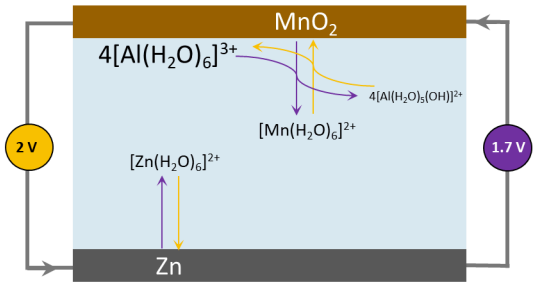
ABSTRACT. Rechargeable aqueous aluminum batteries are the subject of growing interest, but the charge storage mechanisms at manganese oxide-based cathodes remain poorly understood with as many mechanisms as studies. Here, we use an original *in situ* spectroelectrochemical methodology to unambiguously demonstrate that the reversible proton-coupled MnO_2-to-Mn^{2+} conversion is the main charge storage mechanism occurring at MnO_2 cathodes over a range of slightly acidic Al^{3+}-based aqueous electrolytes. In Zn/MnO_2 assemblies, this mechanism is associated with high gravimetric capacity and discharge potentials, up to 560 mAh·g^{-1} and 1.76 V respectively, attractive efficiencies (*CE* > 98.5 % and *EE* > 80%) and excellent cyclability (> 750 cycles at 10 A·g^{-1}). Finally, we conducted a critical analysis of the data previously published on MnO_x cathodes in Al^{3+}-based aqueous electrolytes and identified the universal charge storage mechanism: reversible electrodissolution/electrodeposition of MnO_2.

TOC GRAPHICS



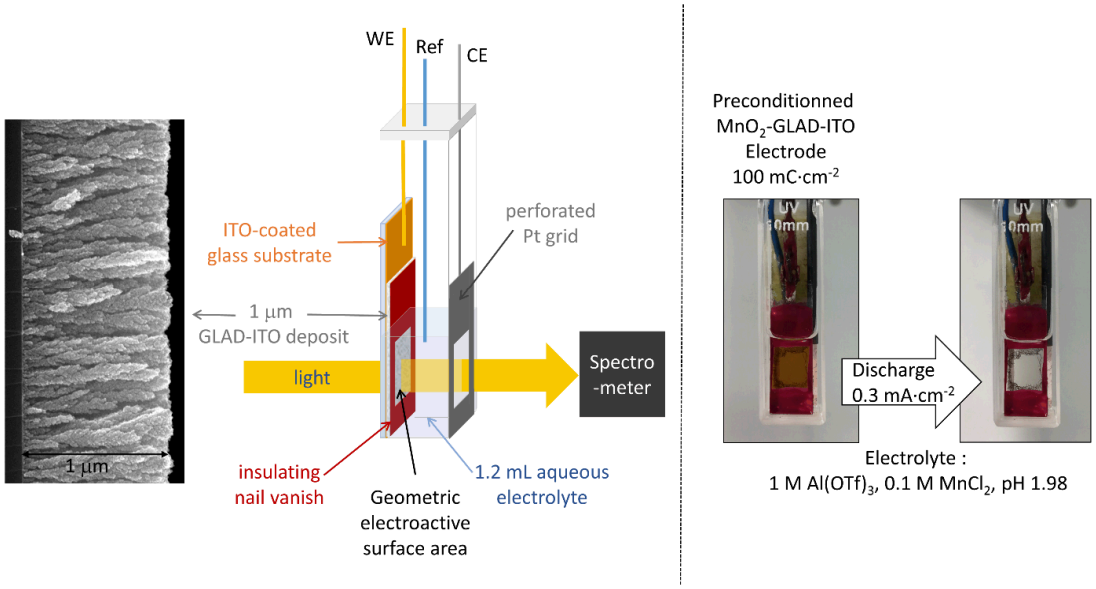
Insertion of earth-abundant multivalent (MV) metal cations (*e.g.*, Mg^{2+}, Zn^{2+} and Al^{3+}) into host electrode materials is currently the subject of much attention due to the promising potential to go "beyond lithium". This is especially true with regard to the development of new insertion-based rechargeable aqueous batteries, which are currently under intensive study due to cost, safety and eco-sustainability considerations.[1,2] However, the real ability of multivalent cations to reversibly insert into redox-active materials, especially metal oxide-based hosts, is still uncertain.[3] Indeed, it has long been believed that the strong electrostatic interaction of MV cations with metal oxide lattices considerably hinders solid-state diffusivity,[4] leading to low electrochemical activity even in the presence of a strong thermodynamic driving force. Moreover, the high solvation energy of MV cations, especially in water, is an additional insertion barrier, adding to the difficulties of MV-ion insertion. Despite all of this, numerous recent works report the reversible insertion of MV cations into metal oxides in the presence of water, and under these conditions, they demonstrate electrochemical performances much better than in pure organic electrolytes.[5–7] However, a growing number of recent studies propose that the attractive performances observed with aqueous MV-ion batteries result from the reversible insertion of protons into the host electrode rather than MV cations. This has been evidenced in particular for VO_2,[8] V_2O_5,[9] $Na_3V_2(PO_4)_2F_3$,[10]and TiO_2[11] electrode materials cycled in either mild acidic Zn^{2+}- or Al^{3+}-based aqueous electrolytes. Moreover, in our previous work on TiO_2, we demonstrated that the source of protons in mild aqueous electrolytes was neither water nor H_3O^+, but the hexaaquo MV complexes (*e.g.*, $[Zn(H_2O)_6]^{2+}$, $[Al(H_2O)_6]^{3+}$) which spontaneously form in water to produce weak Brønsted acids.[11] More recently, we have also shown that the hexaaquo cations $[Zn(H_2O)_6]^{2+}$ and $[Mn(H_2O)_6]^{2+}$, commonly present in the aqueous electrolytes of Zn/MnO_2 batteries, can act as proton sources to trigger the electrodissolution of MnO_2 into Mn^{2+}.[12] These studies underline the crucial, but little-

known role played by the weak acidity of hydrated MV ions on the charge storage mechanisms at metal oxide electrodes. An illustration is provided by the trivalent Al^{3+} cation, which has recently been promoted for "rechargeable aqueous aluminium batteries", wherein an aluminium (or zinc) anode is paired with a MnO_x cathode in an Al^{3+}-based aqueous electrolyte.[13–18] A collective issue with these works, however, is the disparate variety of charge storage mechanisms and cathode compositions that are proposed. Indeed, some works suggest the reversible insertion of MV cations (Al^{3+} or Zn^{2+}) into either the pristine K_xMnO_2 phase[16] or an Al_xMnO_2 phase generated from a solid Mn_3O_4,[14] MnO[18] or MnO_2[17] precursor. Other reports assume a reversible conversion process, either solid-solid (*i.e.*, MnO_2-to-Mn_3O_4)[13] or solid-liquid (*i.e.*, Al_xMnO_2-to-Mn^{2+}),[15] without clearly describing the role and source of protons.

In light of the numerous and contradictory mechanistic propositions, our objective with the present work is to decipher the exact role of Al^{3+} ions in the reversible charge storage mechanism of MnO_x cathodes immersed in Al^{3+}-based aqueous electrolytes. As we will see, our results unambiguously support a mechanism based on the reversible proton-coupled electrodissolution of solid MnO_x materials into soluble Mn^{2+} ions for a wide range of Al^{3+}-based electrolyte compositions, and they challenge the previously-reported charge storage mechanisms which are critically reviewed here.[13–18]

In the present work, MnO_x is quantitatively monitored during galvanostatic cycling by *in operando* UV-visible spectroelectrochemistry. This method was previously used to characterize amorphous MnO_2 within a 3D mesoporous transparent electrode (*i.e.,* a 1 μm-thick nanostructured ITO film deposited by glancing angle deposition (GLAD), over a flat ITO-coated glass substrate – see Scheme 1).[12,19] Here, we prepare similar MnO_2-GLAD-ITO electrodes (see Experimental Section for details and Fig. S1 and S2)[19] by systematically applying 100 $mC \cdot cm^{-2}$ to the

nanocolumnar GLAD-ITO electrodes, which is equivalent to 48 ± 1 μg·cm^{-2} MnO_2.[19] XRD and XPS analysis of the electrodeposited material show that MnO_2 is amorphous and characterized by an average Mn oxidation state of 3.86.[19] Accordingly, the maximal theoretical gravimetric capacity of these MnO_2-GLAD-ITO electrodes is 574 mA·h·g^{-1}. Their electrochemical reactivity was examined with/without Al^{3+} in a three-electrode cell configuration in different aqueous electrolytes adjusted to pH 2.0 (see Table S1 for chemical compositions). The spectroelectrochemical data associated with the first galvanostatic discharges are given in Fig. 1A and 1B.



Scheme 1. Left: schematic of the *in operando* spectroelectrochemical setup used to monitor a MnO_2-loaded GLAD-ITO electrode (made of a 1-μm thick transparent nanostructured film of GLAD-ITO). Right: photographs of the spectroelectrochemical cell taken at the beginning and end of a galvanostatic discharge experiment performed at a GLAD-ITO electrode loaded *ex situ*.

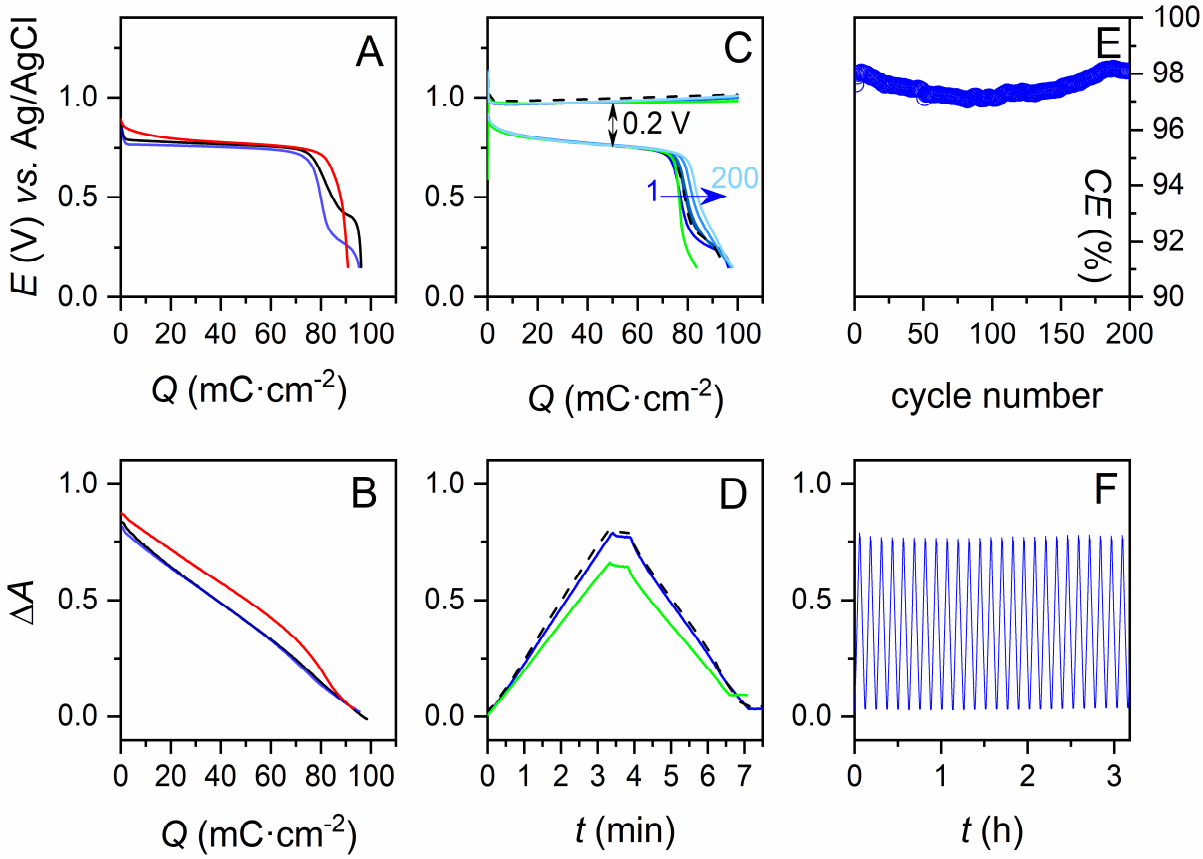


Figure 1. *In operando* spectroelectrochemical characterization of MnO_2-GLAD-ITO electrodes in different aqueous electrolytes (adjusted to pH 2). (A) Galvanostatic curves (rate: 0.3 mA·cm^{-2}) and (B) absorbance variations concomitantly recorded during the first discharge of a MnO_2-GLAD-ITO electrode (loaded *ex situ* with a deposited charge of 100 mC·cm^{2}) immersed in the following electrolytes: (red) 1 M acetic acid + 0.1 M $MnCl_2$ + 2 M KCl, (blue) 1 M $Al(OTf)_3$ + 0.1 M $MnCl_2$, and (black) 1 M $AlCl_3$ + 0.1 M $MnCl_2$. (C) Galvanostatic charge/discharge curves (rate: 0.3 mA·cm^{-2}) and (D, F) absorbance variations concomitantly recorded at a GLAD-ITO electrode cycled in an aqueous electrolyte containing: (blue) 1 M $Al(OTf)_3$ + 0.1 M $MnCl_2$, (dashed black) 1 M $Al(OTf)_3$ + 0.1 M $MnCl_2$, and (green) 1.4 M $Al(OTf)_3$ + 7.1 mg/L MnO (see text for details). (E) Coulombic efficiencies (*CE*) recovered from the continuous galvanostatic experiment reported in (C) and (F).

In a 1 M acetic acid (pH 2.0) electrolyte, the galvanostatic discharge curve is characterized by a well-defined single plateau (red line in Fig. 1A), leading to an areal discharge capacity (C_d) of 92 mC·cm^{-2} (Table S1) close to the *ex situ* deposited charge of 100 mC·cm^{-2} (thus a Coulombic efficiency of CE = 92%). Concomitantly, the absorbance of the electrode decreases almost linearly to near zero (red line in Fig. 1B). These observations are in line with those we have recently reported[19] in a 1 M acetate buffer of pH 5 and support the following proton-coupled electron transfer reaction, in which acetic acid is involved as a proton donor:

$$Mn^{IV}O_2 + 4\ CH_3COOH + 4\ H_2O + 2\ e^- \rightarrow [Mn^{II}(H_2O)_6]^{2+} + 4\ CH_3COO^- \qquad (1)$$

The near complete electrodissolution of MnO_2 is further confirmed by the low m_{MnO_2} value obtained for the discharged electrode (Table S1), indicating that only ~4% of the initially electrodeposited Mn remains on the electrode. As a result, the discharge gravimetric capacity is 530 mA·h·g^{-1}, close to the theoretical value.

The half-discharge potential (E_d) of 0.74 V (*vs.* Ag/AgCl) is significantly higher than that previously reported in a 1 M acetate buffer of pH 5 (E_d = 0.50 V).[12,19] This can be easily explained from the lower electrolyte pH here and the Nernst equation derived from reaction 1 (see eq. S1).[12] However, to accurately interpret the E_d value, it is important to consider that the local pH at the MnO_2/electrolyte interface can differ from the bulk and is indeed expected to rise significantly during the MnO_2 electrodissolution (according to the stoichiometry of reaction 1). Using eq. S1 and assuming that the process remains near thermodynamic equilibrium, the E_d value of 0.74 V translates into a local pH of ~3, thus slightly higher than the bulk pH 2. This agrees with a local conversion of acetic acid into acetate, which, as a function of their respective local activities and pK_a (4.74), determine the local pH (see SI for details).

It is worth noting that at pH 2, the concentration of free protons (*i.e.*, H_3O^+) remains too low (~10^{-2} M) to trigger the reductive electrodissolution of MnO_2 in an inert KCl electrolyte (see Fig. S4 and associated text), whereas at pH 1, the H_3O^+ concentration becomes sufficient (~0.1 M) to complete the proton-coupled electrodissolution of MnO_2 (see Fig. S4 and Table S1). This behaviour is consistent with recent reports for rechargeable aqueous Zn/MnO_2 batteries operating in strongly acidic electrolytes.[20,21] As a consequence for further study, we deliberately avoided the overly concentrated Al^{3+}-based electrolytes (common in the literature) as they leads to very low pHs (Table S2) and participation of H_3O^+ in the discharge process. In Fig. 1A and 1B, the data recorded during the first galvanostatic discharge of MnO_2-GLAD-ITO electrodes in 1 M $Al(OTf)_3$ and 1 M $AlCl_3$ aqueous electrolytes (pH 2) are also overlaid. The shapes and positions of the discharge and absorption curves are almost identical to those recorded in the 1 M acetic acid, the only difference being the appearance of a poorly-defined secondary discharge plateau, located at a lower potential. We do not believe these secondary plateaus are linked to aluminium ions in the electrolyte since they were previously observed in an Al^{3+}-free acidic electrolyte.[21] Alternatively, we suspect it could be related to the denucleation process, which may be more difficult at the end of the discharge. For either Al^{3+}-based electrolyte, a full recovery of the electrode transparency was observed (see pictures in Scheme 1), demonstrating full electrodissolution of MnO_2. This was also corroborated by both the high CE > 96% and small m_{MnO_2} values after discharge (see Table S1). Accordingly, an exploitable gravimetric capacity as high as 550 $mA \cdot h \cdot g^{-1}$ could be achieved, almost identical to the value in 1 M acetic acid. These observations lead to the irrefutable conclusion that we are dealing with a two-electron MnO_2-to-Mn^{2+} conversion mechanism, involving protons (or proton donors) as the charge carriers.

Another interesting feature of the discharge curves in Fig. 1A is their almost identical half-discharge potential values (Table S1), which indicates similar local pHs at the MnO_2 surfaces regardless the nature of the electrolyte. This implies that the proton donors involved in the conversion reactions are weak Brønsted acids of similar strength (*i.e.,* close pK_a). Given that the hexaaquo complex $[Al(H_2O)_6]^{3+}$ has a weak Brønsted acidity (pK_a = 4.9)[22] comparable to that of acetic acid (pK_a = 4.76), we propose by analogy to reaction 1, the following proton-coupled MnO_2-reductive electrodissolution reaction 2 in the Al^{3+}-based aqueous electrolytes:

$$Mn^{IV}O_2 + 4\ [Al(H_2O)_6]^{3+} + 4\ H_2O + 2\ e^- \rightarrow [Mn^{II}(H_2O)_6]^{2+} + 4\ [Al(H_2O)_5(OH)]^{2+} \qquad (2)$$

Once completely discharged, the electrodes were subjected to a galvanostatic charge of 100 $mC \cdot cm^{-2}$ at a rate of 0.5 $mA \cdot cm^{-2}$. The data recorded in 1 M $Al(OTf)_3$ containing 0.1 M $MnCl_2$ are reported in Fig. 1C to 1F (blue curves). During the charge, the potential rapidly stabilizes at 0.98 V, while the absorbance of the electrode increases linearly (Fig. 1D), confirming a steady electrodeposition of MnO_2 to an amount close to that achieved for the electrodes loaded *ex situ*. Interestingly, similar results were obtained with a fresh GLAD-ITO electrode charged *in situ* in the same electrolyte (see black dashed lines in Fig. 1C and 1D), confirming that the MnO_2 electrodeposition remains effective in the Al^{3+}-based electrolyte.

Owing to the conversion mechanism, the electrodeposition of MnO_2 requires the presence of soluble Mn^{2+} ions in the electrolyte. This is commonly achieved by adding a highly soluble inorganic Mn^{2+} salt to the electrolyte. However, as shown below, it can also be achieved from a solid precursor such as MnO, calling into question the recent work of Yan *et al.* on the reversible insertion of Al^{3+} in MnO.[18] Indeed, in agreement with the Pourbaix diagram of manganese, it has

been shown that MnO is prone to dissolve in slightly acidic media.[23] To demonstrate that MnO can effectively dissolve in an Al^{3+}-based electrolyte, we added MnO to a 2 m $Al(OTf)_3$ electrolyte (*i.e.,* the same electrolyte used in [18], see Experimental Section). The resulting electrolyte was then used to cycle a fresh GLAD-ITO electrode. The results in Fig. 1C and 1D (green lines) show the successful electrodeposition/electrodissolution of MnO_2 under these conditions, thereby confirming the spontaneous dissolution of MnO to Mn^{2+} in the Al^{3+}-based electrolyte. XRF analysis of the charged electrode indicates an electrodeposited m_{MnO_2} value of 44 $\mu g \cdot cm^{-2}$, comparable to that obtained with electrodes loaded *ex situ*. We were unable to discern aluminium in the XRF spectrum of the charged electrode, suggesting the absence of an Al_xMnO_2 phase in contrast to what was previously reported.[18]

The continuous galvanostatic cycling of the GLAD-ITO electrode in the 1 M $Al(OTf)_3$ electrolyte containing 0.1 M $MnCl_2$ (see Fig. 1E and data in Table S2) demonstrates a remarkably stable and high *CE* (~97.5 % over 200 cycles), which correlates well with the stable periodic electrode absorbance variations monitored during the first 3 hours of cycling (Fig. 1F). In addition, apart from the secondary discharge plateaus that tend to progressively weaken, the galvanostatic charge/discharge curves almost overlap during cycling. These results are consistent with a complete and highly reversible electrodeposition-electrodissolution conversion process, without significant accumulation of MnO_2 or any other MnO_x material. It is worth noting that aluminium was below the limit of quantification in all the charged and discharged electrodes investigated by XRF. This confirms that the Al_xMnO_2 phase suggested in several works[14,15,17,18] is not formed and also that the electrolyte is properly removed by thoroughly rinsing the electrode with water prior to *ex situ* analysis.

We next investigated the cyclability of the MnO_2-GLAD-ITO electrode in a Zn/MnO_2 cell configuration (two-electrode cell, see Experimental Section for details) with the electrolytes listed in Table S3 (containing Zn^{2+} to allow for the reversible Zn^{2+}-to-Zn conversion reaction at the anode). First, we verified that addition of 0.25 M $ZnCl_2$ to the 1 M $AlCl_3$ + 0.1 M $MnCl_2$ electrolyte does not significantly affect the reversibility and efficiency of the MnO_2-to-Mn^{2+} conversion reaction. This was confirmed from the high *CE* of the galvanostatic cycles (Fig. 2A, 2C and Table S3) and the stable absorbance change recorded during cycling (Fig. 2B). Also in this electrolyte, the Zn/MnO_2 cell delivers an excellent and stable discharge gravimetric capacity of ~560 $mA \cdot h \cdot g_{MnO2}^{-1}$ over 100 cycles (one of the best gravimetric capacities reported for a Zn/MnO_2 cell). The cell also displays a remarkably high discharge voltage (~1.7 V) as well as an excellent energetic efficiency (*EE* > 80% at 10 $A \cdot g^{-1}$).

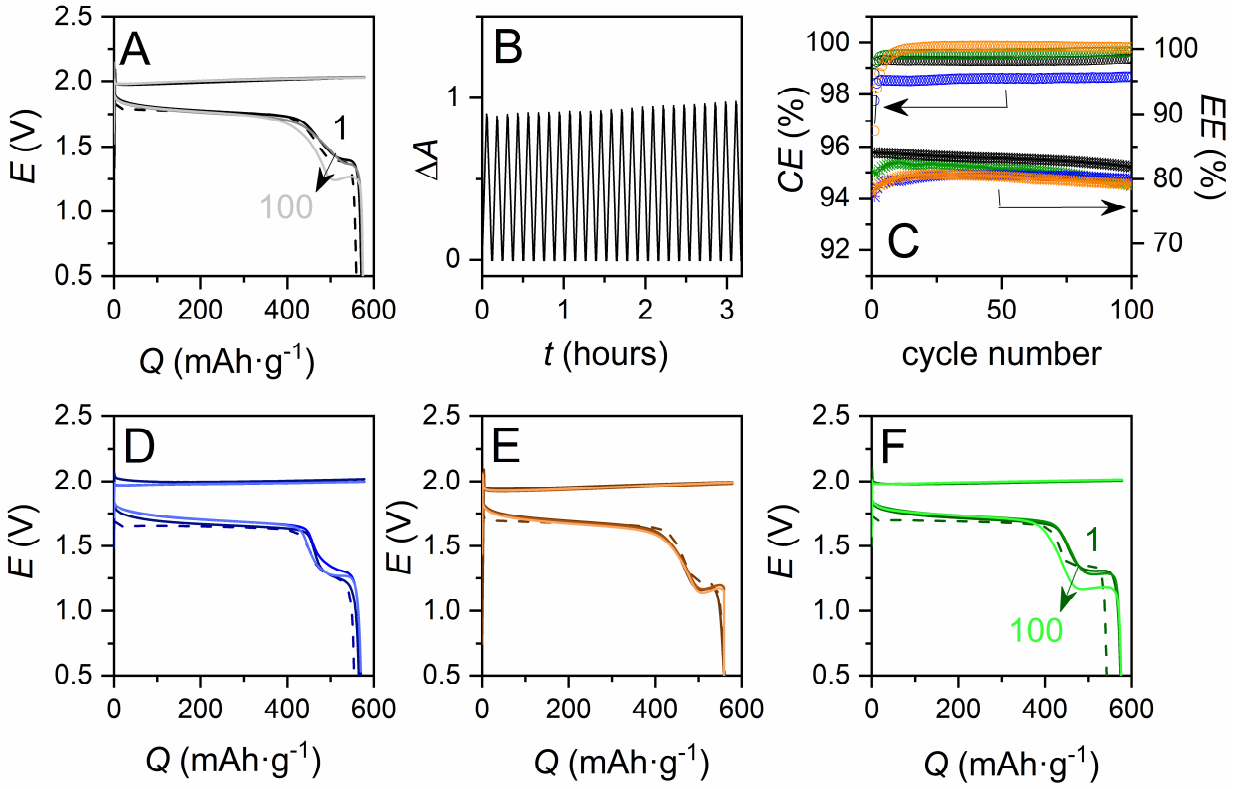


Figure 2. Galvanostatic cycles performed at a Zn foil/MnO_2-GLAD-ITO cell assembly (loaded *ex situ* with 48 $\mu g_{MnO2} \cdot cm^{-2}$) in the presence of the following Al^{3+}-based aqueous electrolytes: (A, B) 1 M $AlCl_3$ + 0.25 M $ZnCl_2$ + 0.1 M $MnCl_2$ (pH 1.90), (D) 1 M $Al(OTf)_3$ + 0.1 M $ZnCl_2$ + 0.1 M $MnCl_2$ (pH 1.77), (E) 1 M $Al(OTf)_3$ + 1 M $Zn(OTf)_3$ + 0.1 M $MnSO_4$ (pH 1.75), and (F) 1.25 M $Al(OTf)_3$ + 0.1 M $ZnCl_2$ + 0.1 M $MnCl_2$ (pH 1.5). The dashed black lines correspond to the 1st galvanostatic discharges (recorded at 0.3 $mA \cdot cm^{-2}$), while the solid lines are galvanostatic charge/discharge cycles (100 cycles at 0.5 $mA \cdot cm^{-2}$ with the 1st, 50th and 100th cycles shown). (C) Cycling performances of the Zn/MnO_2 cell assemblies mentioned in A to F (same color code)

The data presented in Fig. 2 and Table S3 show that the chemical composition of the Al^{3+}-based aqueous electrolytes has little effect on the shape and position of the galvanostatic charge/discharge curves. That all Zn/MnO_2 assemblies have such similar electrochemical features indicates they share a common charge storage mechanism that we attribute to the following dual reversible conversion process:

$$MnO_{2(s)} + 4\ [Al(H_2O)_6]^{3+} + Zn \leftrightarrows Mn^{2+}_{(aq)} + 4\ [Al(H_2O)_5(OH)]^{2+} + 2\ H_2O + Zn^{2+}_{(aq)} \qquad (3)$$

This mechanism is further supported by the excellent gravimetric capacity we have systematically retrieved (*i.e.* > 550 $mA \cdot h \cdot g_{MnO2}^{-1}$), which interestingly is comparable to the value recently achieved in a strongly acidic electrolyte where the reversible proton-coupled conversion of MnO_2 into Mn^{2+} was fully established (see Table 1).[21]

We also tested a bi-cation electrolyte (1 m $Al(OTf)_3$ + 1 m $Zn(OTf)_2$ + 0.1 m $MnSO_4$) with a composition similar to that previously used in [17]. Again, no significant change was observed in the charge/discharge curves (Figure 2E), which confirms that the charge storage mechanism described above remains at work. This is in sharp contrast with the previously proposed mechanism based

on the reversible co-insertion of H^+ and Zn^{2+} in an Al_xMnO_2 phase generated *in situ* (see further comment on pH considerations in the SI).[17] In such bi-cation electrolytes, the cyclability was actually improved with 100% capacity retention over 600 cycles (see Table 1), demonstrating the high reversibility of the dual conversion process.

Table 1. Chemical composition and pH of the aqueous electrolytes used in Zn/MnO_2 or Al/MnO_2 assemblies and the main features of the galvanostatic cycling, *i.e.* rate, half-charge (E_c) and half-discharge (E_d) potentials, maximal discharge capacity, and Coulombic efficiency (*CE*).

electrolyte composition	pH	Anode	Rate ($A \cdot g^{-1}$)	E_d (V)	E_c (V)	*CE*	Maximal discharge capacity ($mA \cdot h \cdot g_{MnO2}^{-1}$)	cathode mechanism	*Ref*
1 M $Al(OTf)_3$, 0.1 M $ZnCl_2$, 0.1 M $MnCl_2$	1.77	Zn	10	1.65	1.99	98.8 % over 250 cycles at 10 $A \cdot g^{-1}$	560	$MnO_2 \leftrightarrow Mn^{2+}$	This work
1 m $Al(OTf)_3$, 1 m $Zn(OTf)_3$, 0.1 m $MnSO_4$	1.75	Zn	10	1.65	1.95	99.7 % over 600 cycles at 10 $A \cdot g^{-1}$	570	$MnO_2 \leftrightarrow Mn^{2+}$	This work
1 M $ZnSO_4$, 1 M $MnSO_4$, 0.1 M H_2SO_4	1	Zn	0.58	1.95	amperometry at 2.2 V	92 % after 1800 cycles at 8.6 $A \cdot g^{-1}$	570	$MnO_2 \leftrightarrow Mn^{2+}$	[21]
1 M $Al(OTf)_3$, 1 M $Zn(OTf)_3$, 0.1 M $MnSO_4$	*ns*	Zn	0.1	~1.55	1.8	~100% over 1000 cycles at 1 C	264	Reversible co-insertion of Zn^{2+} and H^+in Al_xMnO_2	[17]
2 M $Al(OTf)_3$	*ns*	Zn/Al alloy	0.1	1.6	1.8	~75% after 80 cycles at 0.1 $A \cdot g^{-1}$	460	$Al_xMnO_2 \leftrightarrow MnO$ with reversible uptake of Al^{3+}	[18]
2 m $Al(OTf)_3$, 0.1 m $Mn(OTf)_2$	*ns*	T-Al	0.1	1.3	~1.6	~50% after 100 cycles at 0.2 $A \cdot g^{-1}$	310	$MnO_2 \leftrightarrow Mn_3O_4$	[13]
2 M $Al(OTf)_3$, 0.5 M $MnSO_4$	*ns*	T-Al	0.1	1.3→1.15	1.6	~55% after 70 cycles at 0.1 $A \cdot g^{-1}$	554	$Al_xMn_{(1-x)}O_2 \leftrightarrow Mn^{2+}$	[15]
5 M $Al(OTf)_3$	< -0.5	Al	0.03	1.2 & 0.8	1.65	~60% after 65 cycles	467	Reversible Al^{3+} insertion in $Al_{x=0.1}MnO_2$	[14]

ns: not specified

Overall, the present results shed new light on the aqueous aluminium batteries pairing a manganese oxide cathode with an aluminium or zinc anode,[13–18] for which the electrochemical features are gathered in Table 1. It is striking that cells based on identical anodes and electrolytes with similar pHs share similar electrochemical features (notably charge/discharge potentials), a behaviour suggesting thermodynamically equivalent electrochemical processes. On the basis of the present results, it is quite clear that MnO_x to Mn^{2+} conversion is a robust and invariable process independent of the nature of the cathode and/or electrolyte. In view of this behavior, the diversity of mechanisms proposed in the literature (summarized in Table 1) raises questions, as it is very possible that a unified mechanism drives all the Al/MnO_x or Zn/MnO_x aqueous batteries gathered in Table 1.

One may however argue that complementary material characterization techniques are required to better probe our active material and to support the proposed unified charge storage mechanism. However, the characterization techniques based on *ex situ* or *in operando* spectroscopic analysis of the charged/discharged materials, such as XRD, XPS and elemental mapping analysis, are inconveniently blind to the dissolution processes and may mislead the interpretation of the charge storage mechanism. This is especially true for the reduced state Mn^{2+}, which once solubilised in the electrolyte, is no longer detectable by such techniques. Another difficulty is linked to the amorphous state of the back electrogenerated MnO_x material, which unfortunately cannot be characterized by XRD. Despite this, several studies speculate on the *in situ* formation of a layered Al_xMnO_2 phase based on the detection of Al in the XPS spectra and energy dispersive spectroscopy mappings.[14,15,17,18] However, this is insufficient to irrefutably demonstrate the formation of an Al_xMnO_2 phase,[14,15,17,18] and to assert that Al^{3+} can reversibly insert into this phase.[14,18]

Another important aspect that is often improperly considered is that the cyclability of the Zn/MnO_2 batteries improves when sufficient Mn^{2+} (0.1 to 0.5 M) is added into the Al^{3+}-based electrolytes.[13,15,17] Rather than inhibiting the dissolution of Mn^{2+}, we and other groups demonstrated that the role of pre-added Mn^{2+} in the aqueous electrolytes is to act as a reservoir for MnO_2 electrodeposition during charging.[12,24] This is the principle of a conversion battery, where the capacity of the electrolyte has to be taken into account for the energy density calculation.

Some publications report on lower oxidation state manganese oxide cathode materials (*i.e.*, spinel Mn_3O_4 and MnO) capable of cycling in highly concentrated $Al(OTf)_3$ aqueous electrolytes free of Mn^{2+} ions.[14,18] The problem with such oxides is that they tend to spontaneously dissolve in acidic electrolytes,[23, 25] as we have shown here with MnO. Because of the rather high concentration of $Al(OTf)_3$ used in these studies (>2 M at pH < 0, see Table S2), Mn^{2+} is expected to be generated *in situ* from the spontaneous dissolution of the Mn_3O_4- or MnO-based cathode. After a certain time, a significant amount of Mn^{2+} is thus present in these electrolytes, fulfilling the requirements for a reversible MnO_2-to-Mn^{2+} conversion.

Finally, some authors suggest the reversible insertion of multivalent cations (Al^{3+} or Zn^{2+}) in an *in situ* activated layered phase of Al_xMnO_2.[14,17] The present study clearly demonstrates that neither Al^{3+} nor Zn^{2+} can reversibly insert in the active MnO_x phase, which is totally dismantled through the proton-coupled electrodissolution process.

Conclusion

The present study unambiguously demonstrates that the reversible proton-coupled MnO_2-to-Mn^{2+} conversion is the main charge storage mechanism of MnO_x-based cathodes when cycled in Al^{3+}-based aqueous electrolytes. By avoiding excessively high concentrations of Al^{3+} ions

associated with strongly acidic conditions, we highlighted the essential role of the $[Al(H_2O)_6]^{3+}$ complex as a proton donor, allowing exploitation of the 2 electron charge storage capacity of MnO_2 with high cyclability and efficiency. The nature of the counter ions has little effect over the charge storage, making MnO_2-to-Mn^{2+} conversion a robust mechanism that is was likely unknowingly involved in previous studies.

ASSOCIATED CONTENT

(Word Style "TE_Supporting_Information"). **Supporting Information**. Experimental section, Supplementary Figures S1 to SX and supplementary Tables S1 to S3 are provided in the Supporting Information file.

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Notes

The authors declare no competing financial interest.

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