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Vanadium-manganese redox flow battery: Study of Mn(III) disproportionation in the presence of other metallic ions.

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Abstract: The Mn(III)/Mn(II) redox couple with a standard potential of +1.51 V vs. SHE has drawn interest for the design of V/Mn redox flow battery (RFB). However, Mn(III) disproportionation leads to a loss of capacity, an increase of pressure drop and electrode passivation due to the formation of MnO₂ during battery cycling. In this work, we studied the influence of Ti(IV) or/and V(V) on Mn(III) stability in acidic conditions, by formulating 4 different electrolytes at equimolar ratios (Mn, Mn:Ti, Mn:V, Mn:V:Ti). Voltammetry studies have revealed a EC_i process for Mn(II) oxidation responsible for the electrode passivation. SEM and XPS analysis demonstrate that the nature and the morphology of the passivating oxides layer strongly rely on the electrolyte composition. Spectroelectrochemistry highlights the stabilization effect of Ti(IV) and V(V) on Mn(III). At a comparable pH, the amount of Mn(III) losses through disproportionation is decreased by a factor of 2.5 in the presence of Ti(IV) or/and V(V). V(V) is an efficient substitute to Ti(IV) in order to stabilize Mn(III) electrolyte for redox flow battery applications.

Introduction

Renewable energy has attracted both scientific and social attentions over the last decades to face fossil fuel depletion and environmental pollution. The integration of large shares of intermittent energies (*e.g.* solar or wind) into the conventional electrical grid requires the design of energy storage systems to provide a stable supply of power.^[1,2] Among the energy storage solutions, redox flow batteries (RFBs) have drawn considerable attention because they provide a high flexibility by decoupling power and energy.^[3–6] The energy capacity can be tuned by varying the volume of electrolyte, while the power depends on the surface area of the electrochemical cells. A large combination of redox couples^[5] have hitherto been investigated offering large Open Circuit Voltages (OCV): all-vanadium^[7,8] (1.26 V), iron/vanadium^[9] (1.02 V), iron/chromium^[10,11] (1.18V), vanadium/polyhalide^[12,13] (1.43 V), vanadium/cerium^[14–16] (1.4–1.87 V), polysulfide/bromide (1.35 V) and zinc-bromine^[17] (1.85 V). All-vanadium redox flow batteries (VRFB) used V(III)/V(II) and V(V)/V(IV) redox couples as negative and positive sides, respectively, with 2 M H₂SO₄. Although this technology has been commercialized to reach MWh energy storage unit, this battery has difficulties to compete with others energy storage solutions due to a lower energy density and economic reasons such as the highly fluctuating price of vanadium.^[18]

Manganese, the 12th most abundant element on earth, is a transition metal found in ores, in combination with iron, and mainly extracted in South Africa. Among the most common oxidation states (+II, +III, +IV, +VI and + VII), Mn(II) is the most stable. Higher oxidation states are strong oxidizing agents such as permanganate (+VII; MnO_4^-) or manganate anions (+VI, MnO_4^{2-}), or known catalysts for water oxidation (+IV, MnO_2).^[19] The high standard redox potential of the Mn(III)/Mn(II) couple (+ 1.51 V vs. SHE) has attracted interest for the investigation of V/Mn RFB.^[20–22] In this configuration, a cell voltage of 1.77 V ($\text{OCV} = E^\circ_{\text{Mn(III)/Mn(II)}} - E^\circ_{\text{V(III)/V(II)}}$) is expected. As compared to the all-VRFB,^[7,23] the main interest comes from higher energy densities ($35 \text{ Wh}\cdot\text{L}^{-1}$ vs. $20 \text{ Wh}\cdot\text{L}^{-1}$), accounting for a 500 mV higher cell potential. However, cycling performances and battery lifetime remain limited by the instability of Mn(III) in solution, which is disproportionated to Mn(II) and MnO_2 , as given by equation 1:

The formation of MnO_2 particles lead to a reduced mass transport, a higher pressure drop, electrode passivation and irreversible decays in the RFB capacity and power.^[22] To minimize the issues related to disproportionation reactions, higher sulfuric acid concentrations up to 6 M and/or addition of Ti(IV) (TiO^{2+}) to the manganese electrolytes were shown to stabilize Mn(III). Hence, the equilibrium of the disproportionation reaction was displaced and the morphology of the manganese oxide particles modified.^[24–26] Tokuda *et al.* demonstrated by X-ray diffraction and X-ray absorption that formation of Ti- SO_4 bonds in an electrolyte composed of MnSO_4 and TiOSO_4 favors H^+ dissociation from H_2SO_4 and consequently promotes the dissolution of MnO_2 particles with a decrease of the pH.^[27] Recently, a hydrogen/manganese hybrid RFB has demonstrated interesting results maintaining 75% of energy efficiency over 160 cycles at low Mn(II) and Ti(IV) concentrations to prevent MnO_2 formation (0.2 M). However, electrolytes rebalancing was performed every 5 cycles to maintain stable performances.^[28] Most recently, Park *et al.* have proposed two RFBs system composed of multiredox couples V-Mn-Ti^[29] and V-Mn^[30] at both positive and negative sides, reaching energy densities above 35 Wh L^{-1} . In both cases, they observe a significant reduction of MnO_2 particle sizes, especially in the presence of vanadium ions.

Till today, the disproportionation reaction of Mn(III) is not well understood, observations of MnO_2 particles size decreasing are made but no fundamental study has been performed to understand the real effect of Ti and V. Therefore, the applications of manganese electrolyte in RFBs are limited. Several mechanisms were discussed in the literature to describe the oxidation of Mn(II).^[21,29–33] Generally, a $\text{E}_1\text{C}_1\text{E}_2$ mechanism (*e.g.* – electron transfer, irreversible chemical reaction, electron transfer) is considered. The first step consists of the electrochemical oxidation of Mn(II) (E_1 - eq.2):

Then, it was reported that the mechanism for the disproportionation of Mn(III) can differ according to the local proton concentration. In fact, at low pH, Mn(III) disproportionates into Mn(II) and MnO_2 in an irreversible chemical reaction (C_1 - eq.3-4).^[29–35]

At higher pH, Mn(III) could also go through a hydrolysis step to form an Mn-peroxo intermediate, as shown on equation 5:^[32–36]

In this particular case, Mn-OOH can then further be oxidized to MnO₂ through a second electrochemical step (E₂ - eq.6): [29–33]

Those reactions (eq. 4-6) may lead to a chemical and/or electrochemical passivation of the electrode surface [29–33]. The deposition of MnO₂ was described as a nucleation and growth process by Huang *et al.* on graphite electrodes. [34]

Herein, we present a fundamental characterization of various Mn(II) electrolytes in the presence of Ti(IV) and V(V) as a stabilizing agents. Four different electrolytes were studied in high acidic conditions (5 M H₂SO₄) at equimolar ratios: Mn(II), Mn(II):Ti(IV), Mn(II):V(V) and Mn(II):V(V):Ti(IV). Voltammetry was performed in both static and hydrodynamic conditions in order to elucidate the chemical and electrochemical processes associated with the Mn(II) oxidation at the electrode surface. The formation of oxide layers was investigated on both carbon felt and glassy carbon electrodes at low and high acidic concentrations. SEM combined to XPS analysis were used to investigate the morphology and the chemical nature of the oxide. The disproportionation reaction occurring in the bulk was monitored by spectroelectrochemistry, XPS and SEM.

Results and Discussion

Electrochemical study of electrolytes

Electrochemical characterizations of the four electrolytes at equimolar ratio in 5M H₂SO₄ (Mn, Mn:Ti, Mn:V and Mn:V:Ti) were performed by cyclic voltammetry (CV) at 0.01 V·s⁻¹ (Fig.1, A-C) and 1 V·s⁻¹ (Fig.1, B-D).

As shown in Fig.1A for Mn electrolyte, only one anodic peak at +1.72 V vs. SHE was observed and corresponds to the oxidation of Mn(II) into Mn(III), (E₁-eq.2). In this high acidic condition (5 M H₂SO₄), the electrochemical reaction E₂ was not observed, indicating that Mn(III) disproportionates in purely chemical process (eq.3-4). Another reason to claim the absence of E₂ is the low kinetic of Mn-OOH oxidation (eq.6). In fact, Petitpierre *et al.* [32] detected the anodic peak corresponding to E₂ only at temperature above 40°C.

In the cathodic region, two reduction peaks are observed at +1.51 and +1.12 V vs. SHE for Mn. The former peak (+1.51 V vs. SHE) is attributed to the one electron reduction of Mn(III) to Mn(II) (E₁). As Mn(III) is consumed through the chemical step (C_i - eq.3-4), the peak intensity is considerably lower than for the forward peak. At higher scan rate (Fig.B, 1 V·s⁻¹), this peak intensity increases slightly. This effect is characteristic of EC_i processes as the irreversible chemical reaction has less time to occur, and so larger amount of Mn(III) is reduced back at the electrode with less passivation. At the beginning of the reverse scan, an anodic shoulder can be observed at +1.87 V vs. SHE and is induced by the increasing concentration of Mn(II) in the diffusion layer. This rise of concentration comes from the chemical disproportionation reaction of Mn(III) (eq.3).

The second cathodic peak (+1.12 V vs. SHE) is assigned to the reduction of MnO₂ to Mn²⁺ (eq.7):

For Mn:Ti, a similar shape for the CVs was recorded in Fig. 1A and B. The peak attributed to eq.7 was shifted by 30 mV towards cathodic potentials (+1.09 V vs. SHE) and the intensity was lower than for the pure Mn electrolyte.

This suggests an influence of Ti(IV) on the chemical reaction rate (eq. 3-4), that may decrease the formation of MnO_2 . Furthermore, the shoulder at the beginning of the reverse scan (+1.87 V vs. SHE) exhibits a lower anodic current because of a lower rate of disproportionation. It is hypothesized that a dinuclear complex is formed in between Ti(IV) and Mn(III), protecting it from disproportionation. However, no clear spectroscopic signature was reported so far.^[28]

In the presence of vanadium (Fig.1C), additional reversible oxidation and reduction peaks are observed at an apparent standard potential of + 1.1 V vs. SHE attributed to one electron reduction of V(V) to V(IV). The large peak-to-peak potential difference (Fig.1D) is due to the slow kinetics of V(V)/V(IV) redox couples.^[37] Mn(III)/Mn(II) electrochemical reduction is observed at an apparent redox potential of + 1.57 V vs. SHE (Fig 1C). The peak-to-peak potential difference was found to be 20 mV smaller in the presence of vanadium ($\Delta E = 210$ mV for Mn and Mn:Ti ; $\Delta E = 190$ mV for Mn:V and Mn:V:Ti), suggesting a better reversibility. It is worth mentioning the reduction peak potential value was taken at the foot of the wave in all the cases. As compared to Mn and Mn:Ti, the 2-electron reduction of MnO_2 to Mn^{2+} (eq. 7) was not clearly visible because of the overlapping of the V(V) to V(IV) reduction peak. At $1 \text{ V}\cdot\text{s}^{-1}$, a reduction peak was observed at +1.5 V vs. SHE (Fig.1D), accounting for a slower electrode passivation and more favorable electrochemical reduction of Mn(III) to Mn(II). Note that no shoulder around +1.87 V vs. SHE was observed for the pure V(V) electrolyte. This confirms that the origin of the shoulder is due to the sudden increase of Mn(II) concentration following the disproportionation reaction.

Figure 1. iR-corrected cyclic voltammetry of 100 mM (1:1:1) of the different electrolytes: (A&B) Mn and Mn:Ti , (C&D) Mn:V:Ti and Mn:V performed at $10 \text{ mV}\cdot\text{s}^{-1}$ (left chart) and $1 \text{ V}\cdot\text{s}^{-1}$ (right chart) in 5 M H_2SO_4 as supporting electrolyte. (E) Linear sweep voltammetry of the different electrolyte 5 M H_2SO_4 , 100 mM Mn, 100 mM Mn:Ti (1:1), 100 mM Mn:V (1:1) and 100 mM Mn:V:Ti (1:1:1) performed using a glassy-carbon RDE at 1000 rpm and $10 \text{ mV}\cdot\text{s}^{-1}$. The inset shows a zoom of LSV for anodic process at +1.5 V vs SHE. Rotating-disk electrode experiments were carried out for each electrolyte between +1 to +1.8 V vs. SHE at $10 \text{ mV}\cdot\text{s}^{-1}$. The passivation of the electrode by MnO_2 insulating layer prevents the observation of a conventional sigmoidal current. Using Koutecky-Levich equation (see S.I, part A), diffusion coefficients of Mn(II) into the different electrolytes were calculated to be $1.18 \cdot 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$ for Mn electrolyte, which is in good agreement with previous studies.^[37,38] In the case of Mn:V, Mn:V:Ti and Mn:Ti electrolytes, the diffusion coefficients were respectively found to be $3.68 \cdot 10^{-7} \text{ cm}^2\cdot\text{s}^{-1}$, $1.64 \cdot 10^{-7} \text{ cm}^2\cdot\text{s}^{-1}$, $1.66 \cdot 10^{-7} \text{ cm}^2\cdot\text{s}^{-1}$. As the diffusion coefficient depends on $1/a$ (–with a being the ionic radius),

the lower order of magnitude observed in the presence of other metallic ions suggests the formation of a complex between those transition metals. According to the electronic structure of *d* orbitals of Mn(III) (*d*⁴) and the absence of *d* electrons for Ti(IV) and V(V), direct metal-metal bonding is not possible. We anticipate that an oxo-bridge might be responsible for any dinuclear cluster formation, as suggested by Tokuda *et. al.*²⁷

Linear sweep voltammetry was then performed at 1000 rpm up to +2.5 V vs. SHE (Fig. 1E). The inset at +1.5 V vs. SHE shows the oxidation of Mn(II) for the various electrolytes, which corresponds to the E₁C_i mechanisms described previously (eq. 3-5). No current plateau is observed due to electrode passivation by MnO₂, which tends to decrease the current. At + 1.9 V vs. SHE, we observed oxidation peaks at different intensities with the following trend: Mn>Mn:Ti>Mn:V>Mn:V:Ti. This oxidation process is attributed to the oxidation of deposited MnO₂ into the permanganate anion, as shown on equation 8:

The peak current correlates directly to the quantity of MnO₂ deposited after the E₁C_i mechanism. In the presence of vanadium or/and titanium, peak currents were significantly decreased as compared to Mn. This observation suggests a possible complexation between Mn(III) and the different cations, reducing significantly the formation of MnO₂. Finally, the oxidation of the electrolyte to O₂ is observed from + 2.3 V vs. SHE, as shown by the sharp increase in anodic current without diffusion limitation.

The electrochemical characterizations demonstrate a significant influence of V(V) and Ti(IV) cations on the disproportionation reaction of Mn(III).

Surface analysis of electrografted oxide layers

To study further the stabilizing role of Ti(IV) and/or V(V) on the disproportionation process, we investigated the morphology and the chemical nature of the passivating layer formed at the electrode surface using Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). The electrodeposition was performed at +1.8 V vs. SHE onto carbon felt and GC electrodes for each electrolyte in 5 M H₂SO₄. Only few traces of oxide layers were observed by SEM. XPS measurements did not give reliable results due to high signal-to-noise ratio in reason of the low amount of material (Table S2).

To promote the formation of passivating layers, the sulfuric acid concentration was decreased to 50 mM to move the equilibrium of eq.1 towards MnO₂ formation and lower the solubility of oxides particles. For the Mn electrolyte, the carbon fibers were totally covered by MnO₂ flakes with an estimated thickness of 500 nm. The addition of titanium or vanadium reduces considerably the formation of MnO₂, lowering the thickness of the oxide layer below 100 nm (Figure 2).

Figure 2. SEM images of electrodeposited oxide layers on carbon felt electrodes for Mn, Mn:Ti, Mn:V, and Mn:V:Ti electrolytes (3kV, 0.4 nA).

The same experiments on planar GC electrodes were performed and the resulting SEM pictures are shown on Figure 3. The deposition of MnO_2 in the presence of Mn created a thick layer in which cracks are observed. Cactus-like particles above 1 μm of diameter (inset, Fig. 3) are shown as aggregates over the entire electrode surface, suggesting a nucleation/growth process. In the presence of Ti, the amount of deposited oxide layer was reduced. The fluctuating contrast is attributed to variation in chemical composition, suggesting that the passivating layers are thin and do not cover the entire GC sublayers. Interestingly, Mn:V and Mn:V:Ti exhibit oxide layers with different structures, in which a rough surface and particles aggregation are observed on the whole electrode. This suggests another nucleation/growth mechanisms at the electrode surface along with the presence of different oxide species as compared to Mn and Mn:Ti electrolytes.

Figure 3. SEM images of electrodeposited manganese oxide layers on GC electrodes, obtained after electrolysis at +1.8 V vs. SHE, for Mn, Mn:Ti, Mn:V and Mn:V:Ti electrolytes (3kV, 25 pA). The inset on Mn shows the nuclei aggregates on the whole electrode surface.

To determine the chemical nature of the oxide layers observed by SEM, XPS was performed (Figure 4). The relative atomic concentrations (at.%) obtained at 50 mM H_2SO_4 for oxide layers-modified GC electrodes are reported in the Table 1. Binding energies of 642.37 and 654.11 eV are attributed respectively to $\text{Mn}2p_{3/2}$ and $\text{Mn}2p_{1/2}$ orbitals (Fig. 4A – Mn and Mn:Ti). Splitting energy of 4.7eV, obtained for $\text{Mn}3s$ orbitals, correlates with the presence of MnO_2 (Fig.4D).^[39] This is in good agreement with the proposed EC_i mechanism that demonstrates electrode passivation by MnO_2 . For Mn:Ti, MnO_2 was also detected on the electrode surface (Fig 4A and D). Additionally, a

symmetric peak shape of Ti2p orbitals at 458.24 and 463.88 eV, along with a splitting energy of 5.7 eV, are attributed to TiO₂ oxide layers (Fig 4C), accounting for +IV oxidation states. Thus, the passivating layer is a mixture of MnO₂ and TiO₂, with relative atomic concentrations of 90 at.% of Mn and 10 at.% of Ti (Table 1). The presence of TiO₂ may not be a product of the Mn(II)-Ti(IV) oxidation process, discussed in the previous section (Fig.1). TiO₂ was likely formed due to an excess of Ti(IV) that could have been oxidized by the change of acidity of the surface while preparing the samples for SEM and XPS. This suggests that Mn:Ti ratio is not optimal and could be adjusted.

Interestingly, with the presence of vanadium (Mn:V and Mn:Ti:V), no trace of MnO₂ was detected on the surface of the passivating layer. However, a satellite peak at 648 eV is observed in between Mn2p_{1/2} and Mn2p_{3/2} orbitals, which corresponds to the presence of MnO (Fig 4B). This is confirmed by a splitting energy of 5.9 eV in between Mn3s orbitals (Fig.4E), accounting for an oxidation state of +II.^[40] Furthermore, analysis of V2p orbitals resulted in asymmetric peaks at 517.02 and 524.52 eV, that are assigned to 2p_{3/2} and 2p_{1/2} orbitals, respectively. Splitting energy is found to be equal to 7.4 eV, suggesting the presence of V₂O₅ particles.^[41] In the case of Mn:V:Ti, TiO₂ oxide particles were additionally detected, after calculation of the splitting energy in between Ti2p orbitals (Fig. 4C).

For Mn:V, relative atomic concentrations of Mn and V were respectively measured to 89% and 11% (Table 1). The same explanation as for the presence of TiO₂ can be proposed for V₂O₅ detection, suggesting that Mn:V ratio is not ideal. For Mn:V:Ti, 47 at. % of Mn, 15 at. % of V and 37 at.% of Ti were calculated. The higher relative atomic concentration of Ti in the case of Mn:V:Ti compared to the Mn:Ti electrolyte suggests that V may have more affinity in complexing Mn. However, it is worth mentioning that the relative atomic concentrations is quantitative, but it describes a specific region (where the XPS beam scanned the sample) and the results can vary according to the heterogeneity of the passivated layer.

The presence of MnO with vanadium additives is not well understood and seems to be formed only at the electrode surface. We hypothesize that V(V) influences the chemistry at the electrode surface due to an interaction with Mn(II). Although no traces of MnO₂ particles was detected by XPS at the electrode surface, we found them directly in the bulk. This suggests that EC_i process previously described for the oxidation of Mn(II) still occurs in presence of vanadium. Additionally, the peak attributed to MnO₂ oxidation (eq.8) was observed for each electrolyte (Fig. 1E), although this oxidation peak is smaller in the presence of vanadium. The shape of the latter anodic signal differs while adding or not vanadium.

Figure 4. XPS spectra of the electrodeposited manganese oxide layers on glassy carbon electrode for Mn 2p orbitals (A and B), Mn3s orbitals (D and E), Ti 2p orbitals (C) and V2p, O1s orbitals (F). The energy splitting interaction in between orbitals is reported on graph C to F.

Without V(V), a peak comparable to a stripping was recorded, highlighting the presence of a deposited layer of MnO_2 on the electrode surface. When V(V) is added, a signal closer to a plateau is observed, which could describe a diffusion-controlled oxidation due to the MnO_2 particles in suspension.

Table 1. XPS relative atomic concentrations for oxide layers-modified glassy carbon electrodes formed in 50 mM H_2SO_4 as supporting electrolyte.

	Mn	Mn:Ti	Mn:V	Mn:V:Ti
Mn (at.%)	100	90	89	47
V (at.%)	-	-	11	15
Ti (at.%)	-	10	-	37

Study of Mn(III) disproportionation in solution by spectroelectrochemistry, SEM and XPS

Electrochemical investigations and oxide layers structural analysis were useful to address the electrochemical and chemical insights occurring for each electrolyte. Nevertheless, no clear conclusion can be made regarding the Mn(III) stability in solution by studying only the EC_i mechanism. In order to evaluate the stabilizing role of vanadium and titanium in preventing Mn(III) from

disproportionation, spectro-electrochemical studies were performed at high acidic concentration (5 M H₂SO₄).

As shown on the UV-visible spectrum (Fig.5A), the maximum absorption peak of Mn(III) in 5 M H₂SO₄ occurs at 490 nm, which is in accordance with values reported in literature.^[42] After titanium and/or vanadium addition, maximum absorption peaks of Mn(III) are shifted above 500 nm suggesting chemical interactions between those cations, as already reported.^[43] The following values are observed: $\lambda_{\text{Mn(III)}} = 490 \text{ nm}$, $\lambda_{\text{Mn(III)-Ti(IV)}} = 517 \text{ nm}$, $\lambda_{\text{Mn(III)-V(V)}} = 500 \text{ nm}$, $\lambda_{\text{Mn(III)-V(V)-Ti(IV)}} = 506 \text{ nm}$.

As the absorbance of Mn(III) varies according to the nature of the electrolyte, it was necessary to determine the molar absorption extinction coefficient of Mn(III) ($\epsilon_{\text{Mn(III)}}$, λ_{max}) for each solution (Fig. S6 to S9). To calculate those values, various solutions of Mn(III) were prepared by the electrochemical oxidation of 0.1 M Mn(II) solutions in 5 M H₂SO₄. The exact concentration of Mn(III) was confirmed by iodometric titration (see S.I., part C). Finally, the extinction coefficient values were calculated using Lambert-Beer law: $\epsilon_{\text{Mn(III)}} (490\text{nm}) = 108.3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, $\epsilon_{\text{Mn(III)-Ti(IV)}} (517\text{nm}) = 65.8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, $\epsilon_{\text{Mn(III)-V(V)}} (500\text{nm}) = 84.52 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, $\epsilon_{\text{Mn(III)-V(V)-Ti(IV)}} (506\text{nm}) = 52.35 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

Figure 5. UV-visible spectra for 100 mM Mn(III), 100 mM Mn(III)-Ti(IV) (1:1), 100 mM Mn(III)-v, 100 mM Mn(III)-Ti(IV)-V(V) (1:1:1) (left) Concentration of Mn(III) measured by iodometric titration as a function of the amount of charge injected during the electrolysis at +1.8V vs. SHE of 40 mL of a solution of Mn(II) in 5 M H₂SO₄.

To evaluate the disproportionation equilibrium (eq.1) for each electrolyte, solutions of Mn(II) in 5 M H₂SO₄ were electrolyzed at +1.8 V vs. SHE, and the concentration of Mn(III) was monitored by UV-vis spectroscopy. Fig.5B shows the resulting concentration of Mn(III) as a function of the amount of charge injected in the solution during the electrolysis. The black dotted line follows the ideal scenario in which no disproportionation would occur. In this case, the maximal concentration of Mn(III) (equivalent to the initial concentration of Mn(II)) would be reached after injecting exactly 241 C (e.g. – considering 25 mL of a 0.1 M Mn(II) solution in 5 M H₂SO₄). Any deviation below this line results from the disproportionation reaction of Mn(III) (eq.1) or/and other potential side reactions.

Without any other metal ions, the deviation is very significant and Mn(III) concentration reaches a threshold value around 0.075 M. At this concentration, the rate of disproportionation (eq.1) becomes equivalent to the rate of Mn(III) formation (eq.2), maintaining the concentration of Mn(III) constant. This indicates that 25 % of Mn^{3+} produced by electrolysis is involved in the disproportionation process. When Ti(IV) or/and V(V) are added in the electrolyte, Mn(III) concentration values above 0.09 M are reached, resulting in a net shift of the equilibrium towards Mn(III) and confirming the stabilizing effect of Ti(IV) and V(V) additives. In this case, less than 10% of Mn(III) disproportionated. No additional improvement in terms of stabilization was observed by combining the two additives. The main results are reported in Table 2.

Table 2. Summary of values obtained after spectroelectrochemistry for the different electrolytes in 5 M H_2SO_4

	Mn	Mn:Ti	Mn:V	Mn:V:Ti
$\lambda \setminus nm$	490	517	500	506
$\epsilon_{Mn(III)} \setminus$ $M^{-1}cm^{-1}$	108.3	65.8	84.5	52.4
$c_{Mn(III), eq} \setminus$ M	$\approx$ 0.075	>0.090	>0.090	>0.090

Therefore, V(V) was demonstrated as an excellent stabilizing agent for Mn(III) in acidic conditions. Indeed, vanadium was shown to be as efficient as Ti(IV) to reduce Mn(III) disproportionation.

Conclusion

In this work, we investigated the stabilization of Mn(III) towards irreversible disproportionation to Mn(II) and MnO_2 with either Ti(IV) or/and V(V) at equimolar ratio in acidic conditions. Electrochemical characterizations highlight the EC_i mechanism occurring during the oxidation of Mn(II) and resulting in electrode passivation. Hydrodynamic linear sweep voltammetry was performed for Mn, Mn:Ti, Mn:V and Mn:V:Ti, and the diffusion coefficients of Mn(II) were respectively calculated to $1.18 \cdot 10^{-6} cm^2 \cdot s^{-1}$, $1.66 \cdot 10^{-7} cm^2 \cdot s^{-1}$, $3.68 \cdot 10^{-7} cm^2 \cdot s^{-1}$, $1.64 \cdot 10^{-7} cm^2 \cdot s^{-1}$. SEM and XPS experiments were performed to further study the chemical nature and the morphology of the passivating layer at the electrode. To promote the formation of the passivating layer, the experiments were performed at low acidic concentrations. A net decrease in the thickness of the oxide layer was observed with the presence of Ti(IV) or/and V(V). Surprisingly, in the presence of V(V), MnO particles unlike MnO_2 were detected by XPS, suggesting a different chemistry at the electrode surface. However, traces of MnO_2 were still detected in the bulk. Additionally, TiO_2 and V_2O_5 were respectively detected in presence of Ti(IV) and V(V) and might be formed due to an excess of metal ions that could have been oxidized by the change of acidity of the surface.

Spectroelectrochemical analysis were performed for each electrolyte formulation. Without additives, the concentration of Mn(III) reached a threshold value of 0.075M. In the presence of V(V) and Ti(IV),

the threshold concentration increased to a value beyond 0.09 M to onset the disproportionation, confirming the efficient stabilization of Mn(III). Furthermore, the different wavelengths corresponding to the maximum absorbance of Mn(III) between each electrolyte suggest a complexation of Mn(III) with Ti(IV) and/or V(V) via possible oxo-bridge.

Overall, V(V) was observed to enhance the stability of Mn(III) as compared to Ti(IV), which is of high interest for redox flow battery applications. In fact, Mn:V electrolyte could be used instead of Mn:Ti as the positive side of a Mn-V RFB. The stabilization of the Mn(III) would decrease the MnO₂ particles formation and minimize pressure drop, electrode passivation, capacity loss. Then, as observed in the spectroelectrochemical study, the battery might be charged up to 90% SOC without loss of capacity.

Experimental Section

Materials and Methods

Manganese sulfate monohydrate (MnSO₄·H₂O, > 99%), titanium oxysulfate solution (TiOSO₄, ~15 wt. % in dilute sulfuric acid, 99.99% trace metals basis, Sigma-Aldrich), vanadium pentoxide (V₂O₅, > 99.6%) and sulfuric acid (H₂SO₄, 95-97 %) were purchased from Sigma Aldrich and used without further purification. Four different electrolytes were prepared in 5 M H₂SO₄: 0.1 M Mn, 0.1 M Mn:V (1:1), 0.1 M Mn:Ti (1:1), and 0.1 M Mn:V:Ti (1:1:1). Solutions containing vanadium were sonicated and stirred for 2 hours in order to dissolve V₂O₅. For iodometry, anhydrous potassium iodide (KI, 99%) was purchased from Sigma Aldrich and Na₂S₂O₃ sodium thiosulfate pentahydrated (> 99.5%, Fulka) and starch from potatoes ((C₆H₁₀O₅)_n) were purchased from Fulka. Electrochemical experiments were conducted with an Autolab PGSTAT204 (Metrohm) or a Biologic SP-300 potentiostats. Scanning electron microscopy images were performed with a Teneo SEM (FEI, USA) equipped with a Schottky field emission gun. UV/Vis measurements were performed with an Agilent 8453 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was conducted with a VersaProbe II from Physical Electronics.

Electrochemical characterizations

Electrochemical experiments were performed in a 3-electrode setup with a glassy carbon rotating disk electrode (RDE, Metrohm, 0.196 cm²), an Ag|AgCl (KCl sat.) reference electrode, and a platinum counter electrode. The working electrode was polished before each experiment with 1 μm silica polishing solution and immersed in an aqueous solution of isopropanol (50%) in an ultrasound bath for 30 minutes. Static cyclic voltammetry was performed between 0.2 to 2 V vs. SHE at scan rates ranging from 0.005 to 5 V·s⁻¹. Dynamic linear sweep voltammetry was performed with a RDE from 0.2 to 2.5 V vs. SHE at a scan rate of 0.01 V·s⁻¹ and various rotation speeds ranging from 200 to 2500 rpm.

Spectroelectrochemistry

The oxidation reaction of Mn(II) to Mn(III) was monitored by UV-visible spectrophotometry at wavelengths around 500 nm for various electrolyte solutions in 5 M H₂SO₄: 0.1 M Mn, 0.1 M Mn:V (1:1), 0.1 M Mn:Ti (1:1), and 0.1 M Mn:V:Ti (1:1:1). The electrolysis was performed in a H-shape electrochemical cell (H-cell) at + 1.8 V vs. Ag|AgCl (KCl sat.) with a carbon felt working electrode (anode), a carbon felt counter electrode (cathode) and an Ag|AgCl (KCl sat.) reference electrode placed within the anodic compartment. H-cell was composed of a glass frit separator. The anodic and cathodic compartments contained 25 mL of 100 mM Mn(II) sulfate solution and 40 mL of 150 mM VO₂⁺ sulfate solution in 5 M H₂SO₄, respectively. The concentration of Mn(III) along the electrolysis process was monitored by UV-visible spectrophotometry at fixed wavelengths according to the

electrolyte composition: $\lambda_{\text{Mn(III)}} = 490 \text{ nm}$, $\lambda_{\text{Mn(III)-Ti(IV)}} = 517 \text{ nm}$, $\lambda_{\text{Mn(III)-V(V)}} = 500 \text{ nm}$, $\lambda_{\text{Mn(III)-V(V)-Ti(IV)}} = 506 \text{ nm}$. The electrolyte was sampled every 5 minutes from the bulk solution of the positive side using syringe equipped with a 25 mm Yeti HPLC filter (0.22 μm PTFE membrane) to remove the suspended MnO_2 particles. UV-vis spectra background caused by the remaining MnO_2 particles was normalized at 700 nm. The molar adsorption coefficient of Mn(III) in each electrolyte was calculated using a Beer-Lambert relation, and the exact concentration of Mn(III) was determined by iodometric titration. The detailed procedure of iodometry for each electrolyte is detailed in the Supplementary Information section.

Study of manganese oxide formation

The formation of oxides was studied for the various electrolytes. Chronoamperometry experiments were performed in a 3-electrode set-up with different carbon working electrodes (carbon felt and flat glassy carbon), a platinum counter electrode, and an Ag|AgCl (KCl 3M) reference electrode. H-cell electrolysis of Mn(II) was performed at potential value of +1.8 V vs. SHE for 30 minutes. Experiments were conducted twice. Four electrolytes in 50 mM sulfuric acid solution were studied: 10 mM Mn, 10 mM Mn:V (1:1), 10 mM Mn:Ti (1:1), and 10 mM Mn:V:Ti (1:1:1). Scanning electron microscopy (FEI SEM Teneo) of the electro-grafted layers deposited onto carbon felt and glassy carbon electrodes were imaged at 3-5kV, 0.4-0.25nA with lower in-lens, in-column and Everhard-Thronley secondary electron detectors (ETD). Chemical composition of the oxide layers deposited onto the glassy carbon working electrodes were analyzed by XPS. The spectra were calibrated with the C-C bound of the adventitious carbon contamination at 284.8 eV.

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- [1] B. Dunn, H. Kamath, J.-M. Tarascon, *Science* **2011**, 334, 928–935.
- [2] Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, *Chemical Reviews* **2011**, 111, 3577–3613.
- [3] P. Alotto, M. Guarnieri, F. Moro, *Renewable and Sustainable Energy Reviews* **2014**, 29, 325–335.
- [4] C. Zhang, L. Zhang, Y. Ding, S. Peng, X. Guo, Y. Zhao, G. He, G. Yu, *Energy Storage Materials* **2018**, 15, 324–350.
- [5] L. Thaller, *Recent Advances in Redox Flow Cell Storage Systems*, **1979**, NASA TM-79185.
- [6] S. Gentil, D. Reynard, H. H. Girault, *Current Opinion in Electrochemistry* **2020**, DOI 10.1016/j.coelec.2019.12.006.
- [7] D. Reynard, C. R. Dennison, A. Battistel, H. H. Girault, *Journal of Power Sources* **2018**, 390, 30–37.
- [8] M. Rychcik, M. Skyllas-Kazacos, *Journal of Power Sources* **1988**, 22, 59–67.

- [9] W. Wang, Z. Nie, B. Chen, F. Chen, Q. Luo, X. Wei, G.-G. Xia, M. Skyllas-Kazacos, L. Li, Z. Yang, *Advanced Energy Materials* **2012**, 2, 487–493.
- [10] Y. K. Zeng, T. S. Zhao, L. An, X. L. Zhou, L. Wei, *Journal of Power Sources* **2015**, 300, 438–443.
- [11] C.-H. Bae, E. P. L. Roberts, R. A. W. Dryfe, *Electrochimica Acta* **2002**, 48, 279–287.
- [12] M. Skyllas-Kazacos, *Journal of Power Sources* **2003**, 124, 299–302.
- [13] M. Skyllas-Kazacos, *Vanadium/Polyhalide Redox Flow Battery*, n.d., US7320844B2.
- [14] X. Xia, H.-T. Liu, Y. Liu, *Journal of The Electrochemical Society* **2002**, 149, A426.
- [15] B. Fang, *Electrochimica Acta* **2002**, 47, 3971–3976.
- [16] P. K. Leung, M. R. Mohamed, A. A. Shah, Q. Xu, M. B. Conde-Duran, *Journal of Power Sources* **2015**, 274, 651–658.
- [17] E. R. & E. Co. Kantner, E, *Zinc Bromine Redox Flow Battery*, **1985**, US. Patent, 4, 491, 625.
- [18] V. Viswanathan, A. Crawford, D. Stephenson, S. Kim, W. Wang, B. Li, G. Coffey, E. Thomsen, G. Graff, P. Balducci, et al., *Journal of Power Sources* **2014**, 247, 1040–1051.
- [19] A. N. Colli, P. Peljo, H. H. Girault, *Chemical Communications* **2016**, 52, 14039–14042.
- [20] Z. He, G. Jin, C. Gao, Y. Chen, H. Han, J. Liu, *Journal of Renewable and Sustainable Energy* **2014**, 6, 053124.
- [21] F.-Q. Xue, Y.-L. Wang, W.-H. Wang, X.-D. Wang, *Electrochimica Acta* **2008**, 53, 6636–6642.
- [22] H. J. Lee, S. Park, H. Kim, *Journal of The Electrochemical Society* **2018**, 165, A952–A956.
- [23] D. Reynard, H. Vrubel, C. R. Dennison, A. Battistel, H. Girault, *ChemSusChem* **2019**, 12, 1222–1228.
- [24] H. Kaku, Y.-R. Dong, K. Hanafusa, K. Moriuchi, T. Shigematsu, *ECS Transactions* **2016**, 72, 1–9.
- [25] Y.-R. Dong, Y. Kawagoe, K. Itou, H. Kaku, K. Hanafusa, K. Moriuchi, T. Shigematsu, *ECS Transactions* **2017**, 75, 27–35.
- [26] Y.-R. Dong, H. Kaku, K. Hanafusa, K. Moriuchi, T. Shigematsu, *ECS Transactions* **2015**, 69, 59–67.
- [27] K. Tokuda, J. Iihara, Y. Saito, A. Masuno, H. Inoue, *The Journal of Chemical Physics* **2018**, 149, 014503.
- [28] J. Rubio-Garcia, A. Kucernak, D. Zhao, D. Li, K. Fahy, V. Yufit, N. Brandon, M. Gomez-Gonzalez, *Journal of Physics: Energy* **2018**, 1, 015006.
- [29] S. Park, H. J. Lee, H. Lee, H. Kim, *J. Electrochem. Soc.* **2018**, 165, A3215–A3220.
- [30] S. Park, H. Lee, H. J. Lee, H. Kim, *Journal of Power Sources* **2020**, 451, 227746.
- [31] S. Nijjer, J. Thonstad, G. M. Haarberg, *Electrochimica Acta* **2000**, 46, 395–399.
- [32] C. J. Clarke, G. J. Browning, S. W. Donne, *Electrochimica Acta* **2006**, 51, 5773–5784.

- [33] W.-H. Kao, V. J. Weibel, *Journal of Applied Electrochemistry* **1992**, 22, 21–27.
- [34] J.-Ph. Petitpierre, Ch. Comninellis, E. Plattner, *Electrochimica Acta* **1990**, 35, 281–287.
- [35] W. Huang, J. Li, Y. Xu, *Materials* **2017**, 10, 1205.
- [36] L. Moyer, *Advanced Inorganic Chemistry*, World Technologies, S.I., **2014**.
- [37] J. Lawton, S. Tiano, D. Donnelly, S. Flanagan, T. Arruda, *Batteries* **2018**, 4, 40.
- [38] Y. Gorlin, C.-J. Chung, D. Nordlund, B. M. Clemens, T. F. Jaramillo, *ACS Catalysis* **2012**, 2, 2687–2694.
- [39] M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, R. St. C. Smart, *Applied Surface Science* **2011**, 257, 2717–2730.
- [40] V. Di Castro, G. Polzonetti, *Journal of Electron Spectroscopy and Related Phenomena* **1989**, 48, 117–123.
- [41] M. C. Biesinger, L. W. M. Lau, A. R. Gerson, R. St. C. Smart, *Applied Surface Science* **2010**, 257, 887–898.
- [42] K. Maiti, P. K. Sen, A. K. Barik, B. Pal, *J. Phys. Chem. A* **2018**, 122, 5270–5282.
- [43] R. G. Selim, J. J. Lingane, *Analytica Chimica Acta* **1959**, 21, 536–544.