



High energy density $\text{MnO}_4^-/\text{MnO}_4^{2-}$ redox couple for alkaline redox flow batteries†

Cite this: *Chem. Commun.*, 2016, 52, 14039

Alejandro N. Colli,* Pekka Peljo and Hubert H. Girault

Received 6th October 2016,
Accepted 11th November 2016

DOI: 10.1039/c6cc08070g

www.rsc.org/chemcomm

The $\text{MnO}_4^-/\text{MnO}_4^{2-}$ redox couple has a positive redox potential, high electrochemical reversibility and high solubility, up to 3.62 M at room temperature. Careful optimization of the electrolyte composition and the potential limits eliminates the side reactions, making this redox couple an attractive option for alkaline redox flow batteries.

Redox flow batteries (RFBs) are receiving wide attention for large-scale energy storage due to their many attractive advantages including decoupling of energy storage and power output, high coulombic (CE) and energy (EE) efficiencies, and scalability. Among the various options considered, RFBs have become one of the most promising electricity-storage systems to address the intermittency issues of renewable energy sources such as wind and solar.^{1–6} However, they are limited by their low energy density. To solve that problem, the active species are required to have reversible redox behaviour with a redox potential within the electrochemical potential window of the solvent, and large solubility in the electrolytes.

Existing RFBs are mainly based on metal ions dissolved in acidic solutions. They suffer capacity losses due to membrane crossover, electrode corrosion and the occurrence of undesired secondary reactions during battery cycling, which translate into high operational and maintenance costs. Nowadays research efforts focus on cheaper materials, higher energy densities and better energy efficiencies.

In this perspective, alkaline RFBs have the advantages of low self-discharge and low hydrogen evolution rate.⁷ Alkaline solutions allow the use of materials which are cheaper and less susceptible to corrosion compared to those required in acidic condition and, to compensate a lower conductivity of the electrolyte, they can tolerate the use of more conductive metallic three dimensional electrodes, allowing an overall higher energy efficiency.⁸

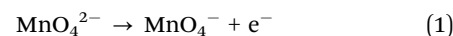
Recently, an alkaline quinone RFB,⁹ an all-iron aqueous RFB¹⁰ and an alkaline RFB based on the coordination chemistry of iron and cobalt¹¹ have been proposed, showing good stability

of compounds, inexpensive raw materials and a lower species crossover in comparison with existing commercial technologies.

The $\text{MnO}_4^-/\text{MnO}_4^{2-}$ redox couple in alkaline media for use as a positive redox couple is attractive for RFBs because it has a positive redox potential ($E^0 = 0.558$ V vs. SHE,¹³ corresponding to 1.38 V vs. RHE at pH 14), high reversibility¹⁴ and high solubility when used as the sodium salt, which results in a battery with a large energy storage capacity of 97 A h dm⁻¹ or 63 A h kg⁻¹ of the electrolyte. Both Mn species are chemically stabilized in highly concentrated OH⁻ solutions.¹⁵ Also, a low crossover rate is expected, due to exclusion of the negative active species by cationic membranes. Fig. 1 shows potential energy densities for different existing negative redox couples in conjunction with current $\text{MnO}_4^-/\text{MnO}_4^{2-}$. It can be seen that the potential energy density could be much higher than existing RFB chemistries.

The redox couple was evaluated at room temperature with NaOH or KOH supporting electrolytes by cyclic voltammetry, rotating disc electrode method on a carbon or platinum disk electrode, and by charge/discharge cycling.

The electrochemical oxidation of manganate(vi) to permanganate(vii), reaction (1), is carried out industrially, but has not before been considered for energy storage applications. Typically, this reaction is performed in an undivided cell with an electrolyte containing potassium hydroxide and potassium manganate at 60 °C at an anode made from nickel or monel, while the cathode is iron or steel.¹⁶



A few studies have been carried out in order to obtain permanganate from manganate in a divided cell made with a Nafion 423 ion exchange membrane¹⁷ or more recently Nafion 417.¹⁸ In both cases, no stability problems were detected.

A second redox couple corresponding to reaction (2) is observed at slightly lower potentials. Both processes can be seen in Fig. 3(A).



It was found that the rate of the electrode reaction (1) is higher than that of electrode reaction (2) under comparable conditions.¹⁹

Laboratoire d'Electrochimie Physique et Analytique, École Polytechnique Fédérale de Lausanne, EPFL, Valais Wallis, Rue de l'Industrie 17, Case Postale 440, CH-1951 Sion, Switzerland. E-mail: anculli@gmail.com

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cc08070g

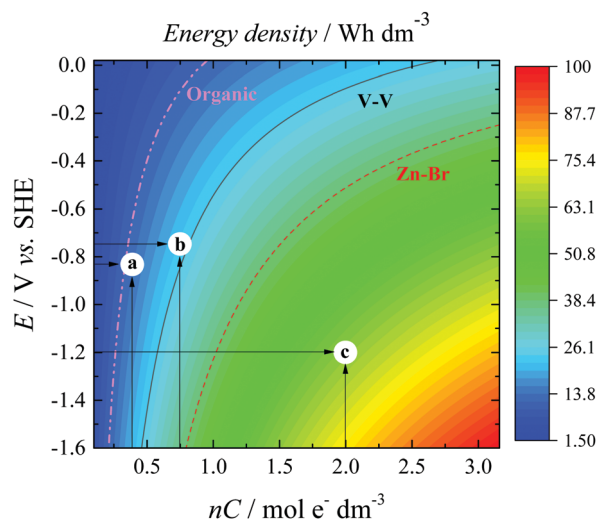


Fig. 1 Contour plots of energy density of alkaline RFBs taking into account Mn(vi)/Mn(vii), as a function of redox potential and concentration of electrolyte of the negative redox couple, (a) Mn(vi)/Mn(vii)–iron–TEA RFB,¹¹ (b) Mn(vi)/Mn(vii)–quinone RFB,⁹ (c) Mn(vi)/Mn(vii)–Zn RFB.¹² Contour lines: maximum energy density of existing RFBs.

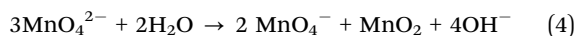
Aqueous potassium permanganate solutions are not perfectly thermodynamically stable at 25 °C, because MnO₂, not MnO₄[−] is the thermodynamically stable form of manganese in water. Thus permanganate tends to oxidize water with the evolution of oxygen and the precipitation of manganese dioxide, which acts to further catalyze the reaction.²⁰ Also, alkaline permanganate solutions have certain inherent drawbacks due to decomposition upon storage for any appreciable period of time. Under extremely alkaline conditions and in the absence of an oxidizable substrate, the permanganate ions tend to slowly oxidize water in the presence of the hydroxyl ions to form manganate(vi) and oxygen gas, as shown by reaction number (3). The further this reaction proceeds in reducing permanganate ions to manganate ions, the less effective is capacity retention of the system for working as a battery.



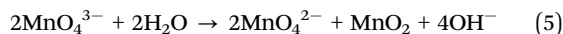
Further reduction of manganate does not occur.²¹ The kinetics of the reaction are relatively slow and permanganate solutions exhibit greatest stability around a neutral pH. The decomposition rates increase below pH 3 or above pH 10.¹⁵

The most striking feature of the kinetic results is the dependence of rate of reaction (3) upon the initial concentration of permanganate. Experimental results shown that the initial rate divided by the initial concentration of permanganate at a fixed concentration of alkali tends to a constant.^{22,23}

Additionally, in aqueous solution, MnO₄^{2−}, disproportionation occurs according to the following reaction,¹⁵ but is extremely low under high alkali concentrations.

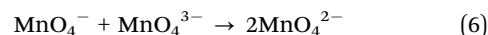


And as stated by Lin *et al.*¹⁴ and Sekula-Brzezinska *et al.*,¹⁹ the following disproportionation, reaction number (5), occurs for moderate alkaline medium:



However, both disproportionation rates decrease with an increase of pH of the solution¹⁹ and are relatively slow under sub-molar alkaline conditions and even slower when alkaline concentration is increased. Ferguson *et al.*²⁴ conclude that neither the colloidal nor the precipitated form of manganese dioxide was a reaction product of the reactions (4) and (5) and that the oxygen loss, due to reaction (3), ceased beyond a certain time for alkali concentrations between 3 and 12.5 molar and temperatures between 50° and 95 °C.

Likewise, when increasing OH[−] concentration above 6 M the following reaction occurs at an immeasurable rate:²⁵



With regard to stability of manganate(vi), in the laboratory, salts are prepared by heating an aqueous solution of alkali metal permanganate in the presence of an excess of strong alkali. The fact that manganate(vi) solutions can be made simply by heating permanganate in concentrated alkaline solution and that the resulting green solutions may then be heated to high temperatures for a long time (24 h) without further change, is a clear evidence that this ion is remarkably stable.

Finally, we have found that for a fixed concentration of alkali, the conversion over time of reaction (3) decreases while increasing permanganate concentrations. Almost full conversion in few days for less than 10 mM permanganate in 7.5 M NaOH to 20% in one month for 4 M permanganate in 7.5 M NaOH. Further investigations can be done in order to reduce the rate of reaction (3) even more.²⁶

In Fig. 2, it can be seen that the redox couple Mn(vii)/Mn(vi) is fully reversible in the range of 0.3–0.75 V vs. SHE (blue curve) for a 5 M NaOH supporting electrolyte. However, if the range of the potential window is extended, a non-reversible behavior is observed due to the electrochemical reaction (2) followed by chemical formation of MnO₂ given by reaction (5) (red curve). It is important to note that this behavior is exacerbated for a lower initial concentration of permanganate due to the decrease of the rate of reaction (6), in the case of extended potential windows.

Fig. 3(A) shows two reversible couples Mn(vii)/Mn(vi) and Mn(vi)/Mn(v) (0.6 and 0.2 V vs. SHE) for different scan rates after 30 cycles. It can be seen that the addition of high alkali supporting electrolyte solves the problem of MnO₂ formation due to reaction (5). Fig. 3(B) shows a cyclic voltammogram of the redox couple at high concentrations (3.62 M of MnO₄[−]). It can be seen that the reversible peak corresponding to reaction Mn(vi)/Mn(v) disappears as a consequence of a fast chemical reaction given by reaction (6) and now the oxidation peak current at ca. 0.65–0.7 V is higher due to the additional Mn(iv) generated in the chemical reaction (6). From the battery point of view, going to a negative potential results in an electrochemical step followed by a chemical one that preserve the charge stored as Mn(vi) when high quantity of Mn(vii) is available. Care should be taken when the amount of Mn(vi) exceeds the amount of Mn(vii), since MnO₂ could be formed.

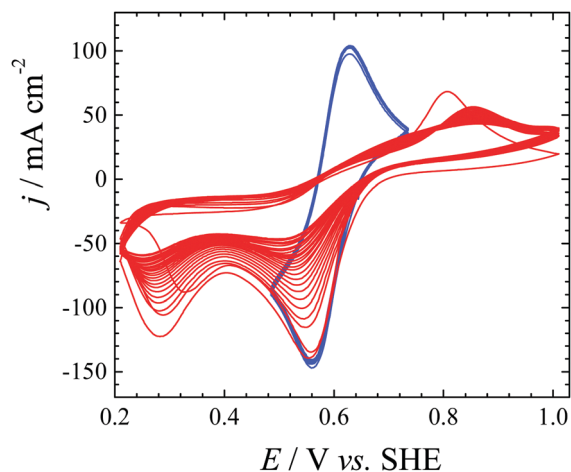


Fig. 2 Cyclic voltammograms on a 3 mm diameter glassy carbon electrode. 3.62 M of MnO_4^- in 5 M OH^- . Scan rate: 20 mV s^{-1} . 30 cycles. Blue curve: reduced potential windows. Red curve: extended potential range.

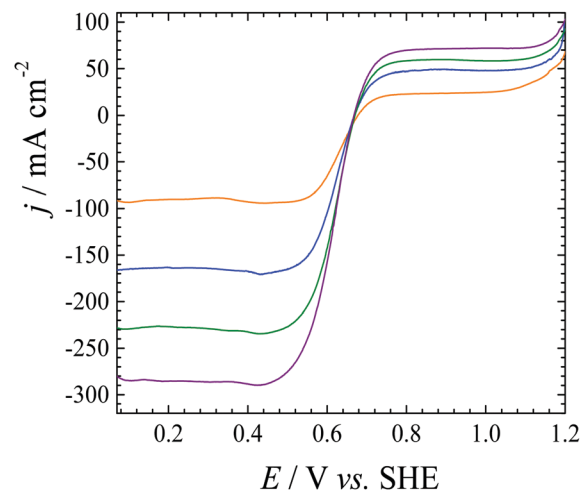


Fig. 4 Polarization curves for the manganate(vi)–permanganate(vii) redox system at a rotating disk electrode made of platinum of 5 mm diameter. Measured after several days of storage. Initial MnO_4^- concentration: 3.62 M of in 7.5 M OH^- as supporting electrolyte. Temperature: ambient. Potential Sweep rate: 1 mV s^{-1} . Rotation rates: 500, 1250, 2000 and 3000 rpm.

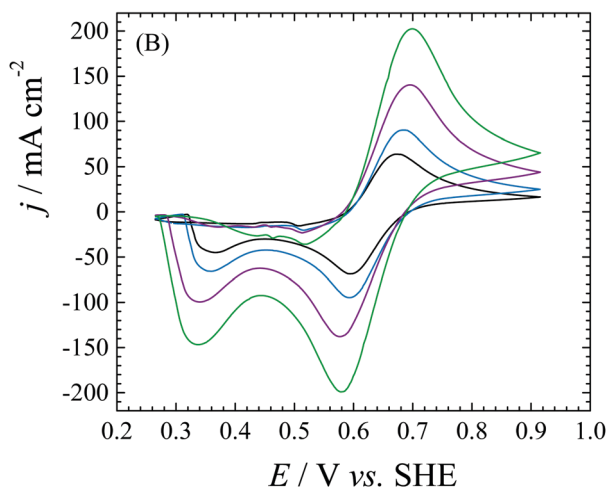
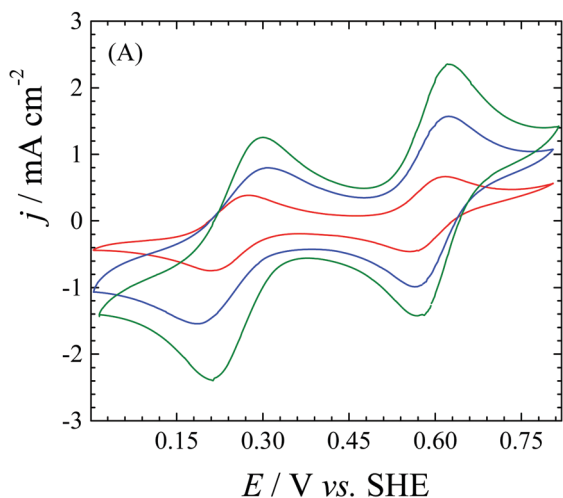


Fig. 3 Cyclic voltammograms on a 3 mm diameter glassy carbon electrode after 30 cycles. (A) 0.01 M of MnO_4^- in 7.5 M OH^- . The scan rates are 10, 50 and 100 mV s^{-1} . (B) 3.62 M of MnO_4^- in 7.5 M OH^- . The scan rates are 10, 20, 50 and 100 mV s^{-1} .

Further research is needed to establish the lower limit of the state-of-charge for the positive electrolyte to avoid MnO_2 precipitation. When comparing Fig. 2 and 3 it can be seen that the reversibility of the system depends on the concentration of MnO_4^- and OH^- as was also stated by Lin *et al.*¹⁴

Fig. 4 shows polarization curves for the manganate(vi)–permanganate(vii) redox system at a rotating platinum disk electrode. Properties of the electrolyte are given in Table 1. The potential sweep rate is 1 mV s^{-1} . It can be seen that the electrochemical reduction of permanganate and oxidation of manganate are both diffusion controlled reactions with a well-defined plateaus. The diffusion coefficients were not calculated due to the large uncertainty in available data for transfer numbers and activity coefficient in such a concentrated solution. Additionally, it can be seen that the relation between reduction and oxidation current densities corresponding to equilibrium values after a month of storage, giving a relation of 4 times permanganate/manganate. Hence, the capacity retention after one month of storage without charge/discharge cycling is 80%.

Fig. 5 presents charge–discharge cycling performance of a positive half-cell, measured with a reference electrode inserted in the positive storage compartment. The cell was assembled with permanganate redox couple, with properties given in Table 1, as positive compartment and NaOH 10 M to produce hydrogen and oxygen evolution as negative one. Nafion 117 cation

Table 1 Experimental properties of the electrolyte

Propriety	Value (28 °C)
Max. MnO_4^- conc. (mol dm^{-3})	3.62
NaOH concentration (mol dm^{-3})	7.5
Dynamic viscosity (mPa s)	24
Density (kg m^{-3})	1.55×10^3
Conductivity (mS cm^{-1})	270

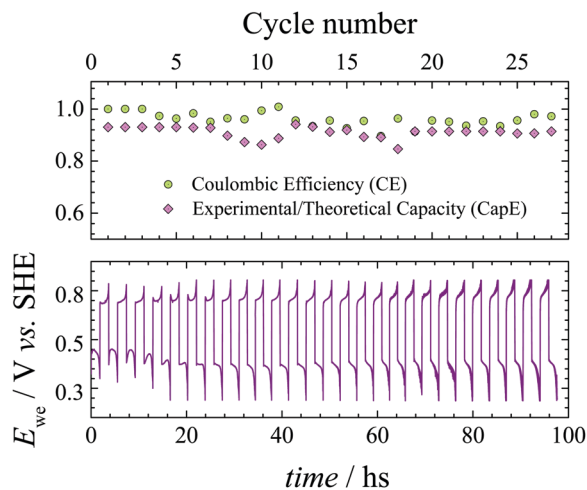


Fig. 5 Upper part: Coulombic and capacity retention efficiencies for each cycle. Lower part: IR corrected cycling behaviour measured as electrode potential vs. SHE.

exchange membrane, permeable to Na^+ , was used to separate both compartments. The upper part of Fig. 5 shows the coulombic and capacity efficiencies (taking into account the maximum theoretical capacity of 1.57 A h) vs. cycling numbers for the $\text{MnO}_4^-/\text{MnO}_4^{2-}$ redox couple at 100 mA cm^{-2} current density in a continuous filter-press electrochemical cell with a flow rate of 35 ml min^{-1} for cathodic and anodic compartments. Although, in this experiment crossover was just from the positive side to the negative, the half-cell demonstrated a quite stable cycling retention with a CE average of 95% through the cycling. After 27 cycles (100 h) the capacity retention was 97%. Additionally, the lower part of Fig. 5 shows the potential of working electrode vs. SHE as a function of time. It can be seen that it took some cycles to reach steady state and in last cycles the system behaved noisily as a consequence of degradation of reference electrode. It is observed that compared with the theoretical capacity, the loss ratio of capacity is really low, indicating an optimal cell behaviour (chemical stability).

Finally, it is worth noting that one has to be very careful about which materials are used to store the reactants and carry out the reaction, since those materials can catalyse MnO_2 formation. We found problems with some plastic tubes and composite carbon materials.

In summary, we demonstrate the performance of the $\text{MnO}_4^-/\text{MnO}_4^{2-}$ redox couple in alkaline electrolyte for use in RFBs. Permanganate is a promising positive redox couple for alkaline RFBs, potentially enabling cost effective stationary storage of renewable energy, highlighting the ability of permanganate to function as stable positive electrolyte for using in redox flow batteries in alkaline solution, helping to resolve serious cost,

corrosion and safety concerns of previous flow batteries chemistries. However, special care should be taken in using different materials to store and produce the electrochemical reaction. Finally, during discharge, care must be taken to prevent the positive half-cell potential going into too negative range, in order to avoid MnO_2 formation. Further experiments are required to test the long-term stability and energy efficiency of this redox couple, and in conjunction of existing redox couples for the negative side.

Notes and references

- M. L. Perry and A. Z. Weber, *J. Electrochem. Soc.*, 2016, **163**, A5064–A5067.
- P. Alotto, M. Guarnieri and F. Moro, *Renewable Sustainable Energy Rev.*, 2014, **29**, 325–335.
- G. L. Soloveichik, *Chem. Rev.*, 2015, **115**, 11533–11558.
- A. Z. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick and Q. Liu, *J. Appl. Electrochem.*, 2011, **41**, 1137–1164.
- C. R. Dennison, H. Vrabel, V. Amstutz, P. Peljo, K. E. Toghil and H. H. Girault, *Chimia*, 2015, **69**, 753–758.
- V. Amstutz, K. E. Toghil, F. Powlesland, H. Vrabel, C. Comninellis, X. Hu and H. H. Girault, *Energy Environ. Sci.*, 2014, **7**, 2350–2358.
- G. B. Adams, *Electrically rechargeable battery*, US4180623 A, 1979.
- G. Kreysa, *Chem. Ing. Tech.*, 1983, **55**, 23–30.
- K. Lin, Q. Chen, M. R. Gerhardt, L. Tong, S. B. Kim, L. Eisenach, A. W. Valle, D. Hardee, R. G. Gordon, M. J. Aziz and M. P. Marshak, *Science*, 2015, **349**, 1529–1532.
- K. Gong, F. Xu, J. B. Grunewald, X. Ma, Y. Zhao, S. Gu and Y. Yan, *ACS Energy Lett.*, 2016, **1**, 89–93.
- N. Arroyo-Currás, J. W. Hall, J. E. Dick, R. A. Jones and A. J. Bard, *J. Electrochem. Soc.*, 2015, **162**, A378–A383.
- L. Zhang, J. Cheng, Y.-s. Yang, Y.-h. Wen, X.-d. Wang and G.-p. Cao, *J. Power Sources*, 2008, **179**, 381–387.
- P. Vanýsek, *Electrochemical Series*, in *CRC Handbook of Chemistry and Physics*, ed. W. M. Haynes, CRC Press/Taylor and Francis, Boca Raton, FL., 2015, pp. 5-80–5-91.
- S.-C. Lin, Y.-Y. Wang, C.-C. Wan and J. C. Chang, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 3372–3376.
- A. H. Reidies, *Manganese Compounds*, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000, pp. 223–244.
- D. Pletcher and F. C. Walsh, *Industrial Electrochemistry*, Chapman and Hall, London, 2nd edn, 1993.
- P. Cox, D. Pletcher and R. P. S. Saluja, *Electrochim. Acta*, 1991, **36**, 173–177.
- K. Subramanian, K. G. Gomathi and K. Asokan, *Ind. Eng. Chem. Res.*, 2008, **47**, 8526–8532.
- K. Sekula-Brzezińska, P. K. Wrona and Z. Galus, *Electrochim. Acta*, 1979, **24**, 555–563.
- K. Pisarczyk, *Manganese Compounds*, in *Kirk Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Hoboken, NJ, 5th edn, 2005, vol. 15, pp. 566–629.
- J. W. Ladbury and C. F. Cullis, *Chem. Rev.*, 1958, **58**, 403–438.
- M. C. R. Symons, *J. Chem. Soc.*, 1953, 3956–3961, DOI: 10.1039/JR9530003956.
- M. C. R. Symons, *J. Chem. Soc.*, 1954, 3676–3679, DOI: 10.1039/JR9540003676.
- R. H. Ferguson, W. Lerch and J. E. Day, *J. Am. Chem. Soc.*, 1931, **53**, 126–137.
- A. Carrington and M. C. R. Symons, *Chem. Rev.*, 1963, **63**, 443–460.
- J. L. Duvall, *Stabilization of alkaline potassium permanganate solutions*, US3210284 A, 1965.