Electronic Supplementary Information

High energy density MnO_4^-/MnO_4^{2-} redox couple for alkaline redox flow batteries

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Chemicals

All chemicals were used as received without further purification. All aqueous solutions were prepared with ultra-pure water (Millipore Milli-Q, 18.2 MΩ·cm). Sodium permanganate solution in H_2O ($MnNaO_4$, 40% wt %) was purchased from ALDRICH. Sodium hydroxide (NaOH, 99+%p.a.) was purchased from chemPUR. Potassium permanganate ($KMnO_4$, 99%+) were provided by Fluka and Potassium hydroxide (KOH, 85%+) was purchased from Fisher Scientific UK.

Physical measurements

Density was measured by weighing a known volume of solution with an XS205DU (Mettler-Toledo International Inc., Switzerland) analytical balance. Dynamic viscosity was measured by a Vibro Viscometer SV-10 (A&D Company Limited, Japan), and conductivity was measured with the help of Impedance spectroscopic technic by a BioLogic SP-300 (Bio-Logic, France) using in an homemade cell that was calibrated with NaOH solutions of known concentration.

Electrochemical experiments

Cyclic voltammograms (CVs) were recorded under ambient aerobic conditions using a PGSTAT101 (Metrohm, the Netherlands) and a BioLogic SP-50 (Bio-Logic, France) potentiostats. Three electrode experiments were performed with glassy carbon or Platinum electrodes (radius 2.5 mm) with Ag/AgCl/(3 M KCl) reference and a platinum counter electrode.

Polarization curves with a rotating ring-disk electrode (RRDE) with a Autolab Motor Control Unit (Metrohm, the Netherlands) where the ring was left inactive during the experiment were recorded under ambient aerobic conditions using a PGSTAT100 (Metrohm, the Netherlands) potentiostat. Three electrode experiments were performed with glassy carbon or platinum disc electrodes (radius 5 mm) with Ag/AgCl/(3 M KCl) reference and a platinum counter electrode.

The electrochemical performance of the battery was tested in a recirculating filter-press configuration, with carbon felt electrodes on both sides, in a three-electrode set-up with Ag/AgCl/(3 M KCl) reference electrode positioned in the positive reservoir. The composition of positive side is given in Table 1, while the composition of negative side was 10 M NaOH. Both reservoirs had 16.5 ml of solution. The applied current density was 100 mA/cm^2 and the geometrical area of electrodes were 2 cm x 4 cm while the thickness of the felt was 3 mm. The flow rate was 35 ml min^{-1} by means of a high precision multichannel peristaltic pump (ISMATEC, Germany). The ohmic resistance was calculated with a current step measurement, where a current step from 0 to 10 mA was taken at the time of 10 ms after the first charge and discharge cycle. It is well known that there will be an ohmic potential drop along the electrode thickness[1]

but the purpose of the paper is to present the chemical and electrochemical behavior of the Mn(VI)/Mn(VII) redox couple for using as a positive side of RFB, thus, experiments were corrected for the IR drop to describe the theoretical potential performance of the redox couple without taking into account the performance of the cell. Anyway, in Fig. S1 it is also presented E_{we} as a function of time without IR compensation as supplementary information.

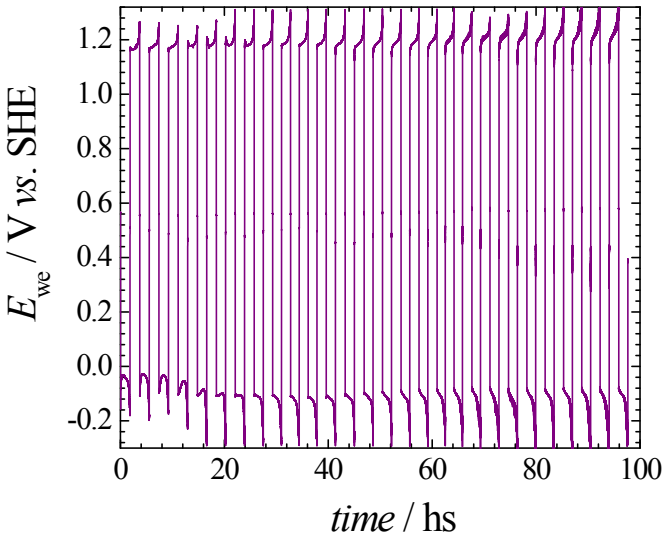

Fig. S1 Cycling behavior measured as electrode potential vs. SHE without IR compensation

References

1. A. N. Colli and J. M. Bisang, *Electrochim. Acta*, 2015, **154**, 468-475.