Supporting Information

Chloride Supporting Electrolytes for All Vanadium Redox Flow Batteries

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Thermodynamic analysis of chlorine gas evolution

To further examine the potential issue of chlorine gas evolution, we conducted thermodynamic analysis. Equilibrium chlorine concentration in the positive solution for the 2.3 M V / 10 M chloride system was calculated using HSC Chemistry® 6.1 program, based on the following reaction:

$$2VO_2^+ + 2Cl^- + 4H^+ \rightleftharpoons 2VO^{2+} + Cl_2(g) + 2H_2O \quad (1)$$

Below 90% SOC, equilibrium chlorine concentration is very low even at 50°C, although it increases rapidly as SOC closing to 100% (see Fig. S1). In practical operation ranges of SOC (20 to 80%), chlorine concentration is negligible even at 50°C and should not be an issue under

normal operating conditions. This is further confirmed by comparison of the equilibrium potential of VO^{2+}/VO_2^+ at the positive side with that of Cl^-/Cl_2 (see Fig. S2). This also indicates that V^{5+} is thermodynamically stable except for near 100% SOC. It should be noted that this thermodynamic gives qualitative insight because of unknown thermodynamic information of the vanadium chlorine complex but it is expected that the chlorine complex formation may decrease chlorine concentration due to the decreased free chlorine concentration. Surprisingly, this analysis is consistent with observation of a negligible pressure change in a fully charged positive reservoir with the 2.3 M V/ 10 M chloride solution at ambient temperature (see Fig. S3). It should be noted that full or over charging should be avoided in the chloride system to avoid potential chlorine evolution, especially at elevated temperature.

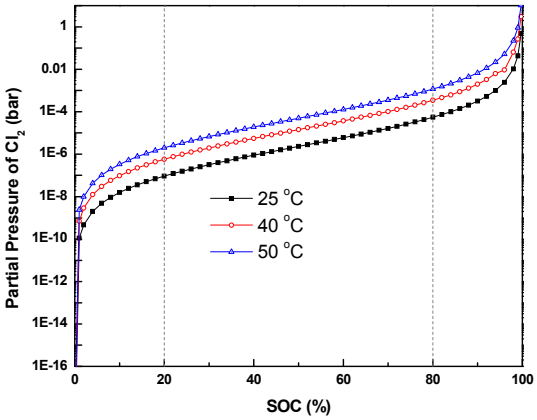

Fig. S1 Equilibrium chlorine concentration in the positive electrolyte of the 2.3 M V / 10 M Cl solution at different temperatures.

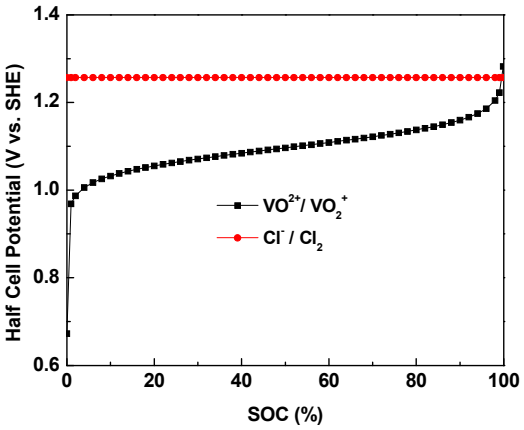

Fig. S2 Equilibrium potential of two half cell reactions in the 2.3 M V / 10 M Cl solution at ambient temperature.

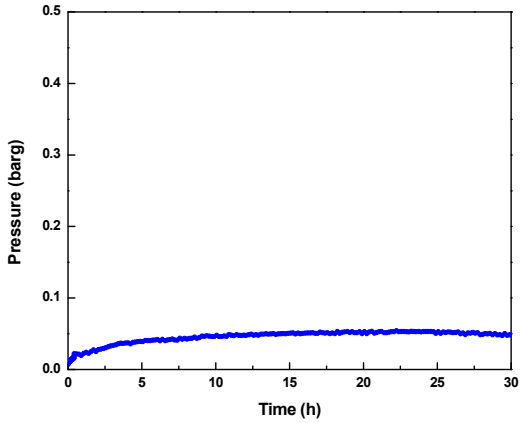

Fig. S3 Pressure change of the fully charged positive electrolyte in the 2.3 M V / 10 M Cl solution at ambient temperature.