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## Anion effects on the redox kinetics of positive electrolyte of the all-vanadium redox flow battery

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### ABSTRACT

The  $\text{VO}^{2+}/\text{VO}_2^+$  redox reaction takes place in the catholyte solution of the all-vanadium redox flow battery (VRFB), one of the few options to electrochemically store energy from intermittent renewable sources on a large scale. However, the sluggish redox kinetics of the  $\text{VO}^{2+}/\text{VO}_2^+$  couple limit the power density of the VRFB, which increases the footprint of the power converters and increases capital costs. Therefore, catalysis of the redox reaction and a deeper understanding of its intricate reaction pathways is desirable. The kinetics of the  $\text{VO}^{2+}/\text{VO}_2^+$  redox reaction have been investigated in 1M sulfuric and 1 M phosphoric acid by cyclic voltammetry, chronoamperometry, electrochemical impedance spectroscopy and flow battery tests. It was found that in 1 M phosphoric acid the electron transfer constant  $k_0$  is up to 67 times higher than in 1 M sulfuric acid. At higher over-potentials the determined currents match for the two electrolytes. This over-potential dependent difference in electron transfer constant is explained by variable contributions from three reaction mechanisms for the oxidation of  $\text{VO}^{2+}$  to  $\text{VO}_2^+$ , and by the presence of adsorbed intermediates for the reduction of  $\text{VO}_2^+$ . This study shows that the redox kinetics of the  $\text{VO}^{2+}/\text{VO}_2^+$  can be considerably accelerated by altering the chemical environment of the vanadium ions, and that this effect can also be transferred into a flow battery.

### 1. INTRODUCTION

The all vanadium redox flow battery (VRFB) has become increasingly important as energy storage for renewable energies due to progressive global warming in recent years. The energy storage is based on the conversion of electrical into chemical energy in the form of soluble redox pairs. Compared to other energy storage systems, the VRFB offers essential

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