

## Aqueous Semi-Solid Flow Cell

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Low-cost and scalable energy storage is vitally important for an electric grid with increasing integration of renewable energy sources such as wind and solar.<sup>1-3</sup> Various novel energy storage technologies have been proposed to improve grid reliability and utilization, including high energy density flow batteries,<sup>4-7</sup> aqueous Li-ion,<sup>8,9</sup> Na-ion,<sup>10-12</sup> and K-ion<sup>13,14</sup> batteries. Flow batteries, which store active electrochemical “fuel” in external reservoirs and pump them into an ion-exchange/electron-extraction power stack to deliver electricity, are considered promising candidates. The inherent flexibility in the architecture of such devices decouples energy and power, which can be exploited to design inexpensive large-scale systems. To meet long-term performance and cost requirements for grid storage, a system-level cost of about \$100/kWh is desired.<sup>1</sup> Amongst flow battery systems, one of the most well-developed is the vanadium redox battery (VRB), which has 40 Wh/L reactants and 20-35 Wh/L at the system level.<sup>15</sup> Projected system costs currently range between \$300-\$800/kWh for VRBs.<sup>2,16</sup>

Accordingly, alternative strategies are sought to increase the energy density of flow batteries and decrease system-level cost.<sup>4-7</sup> Duduta et al.<sup>4</sup> demonstrated a novel approach, the semi-solid flow cell (SSFC), in which the nominal molar concentration of the flow electrodes (also known as catholyte and anolyte) is markedly increased by integrating solid-state intercalation compounds into a flowing, mixed-conducting suspension.<sup>4</sup> This approach is differentiated from all previous flow batteries by imparting electronic conductivity to the flow electrodes themselves, through the use of a conductive nanoparticle suspension, in contrast to the conventional case where the electronically insulating solutions undergo redox reactions only upon contact with current collectors (typically a porous carbon). The SSFC approach has been explored to date only for non-aqueous Li-ion chemistry,<sup>4,7,17,18</sup> where the combination of higher effective molarity and higher cell voltage in principle allows energy density to exceed that of aqueous flow batteries by over ten-fold.

An SSFC based on aqueous chemistry is of interest for scalable low-cost storage, despite the lower cell voltage compared to their non-aqueous counterparts. A number of alkali metal-ion (Li, Na and K) systems have exhibited characteristics compatible with long-term grid storage applications.<sup>8-14</sup> Based on the solid reactants alone, the energy densities of the aqueous Li-ion electrode couples are 100-300 Wh/L. At 30-50 vol% solids, suspensions of these active materials would at least double the volumetric energy density of VRBs. Other factors may also contribute to lower system cost. For example, the cost breakdown for the base-case VRB analyzed by Zhang et al. included 37% from electrolyte (vanadium ions and sulfuric acid) and 31% from stack components (ion-exchange membrane, electrodes and carbon felt).<sup>19</sup> Comparing the major component costs for A-SSFCs and VRBs, industrial grade vanadium is priced at \$20/kg,<sup>19</sup> while lithium-ion battery electrode materials are around \$10-15/kg and their sodium counterparts are even cheaper.<sup>20</sup> The aqueous electrolyte adds negligible cost. Another major cost of VRBs is the ion-exchange membrane for \$500/m<sup>2</sup>,<sup>19</sup> while A-SSFC separators cost only \$2/m<sup>2</sup>.<sup>20</sup>

In this paper, the LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/LiFePO<sub>4</sub> (LTP/LFP) couple is used to demonstrate for the first time an aqueous semi-solid flow cell (A-SSFC). In order to interpret the coupled electrochemical

and advective response inherent to SSFCs, rheological and transport properties of the suspensions are measured, and used to guide computational modeling of charge/discharge behavior with concurrent non-Newtonian flow. Sources of inefficiency resulting from flow-induced equilibration and chemical side reactions are separated. High coulombic efficiency is demonstrated, and operating conditions (including the amount and rate of pumping) for optimal round-trip coulombic efficiency are determined. A main remaining challenge for practical application is shown to be the side reactions prevalent in aqueous Li-ion chemistry, including cathode stability and anode-mediated hydrolysis.

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