Electronic Supplementary Information

A Low-Dissipation, Pumpless, Gravity Induced Flow Battery

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Yield Stress Fluid Modeling

Yield stress fluids can be modeled using simple generalized Newtonian fluids models\(^1\). Typical models include the Bingham plastic model where the stress is the sum of a yield stress and a linear plastic response and the Herschel-Bulkley model where the stress is the sum of a yield stress and a power law plastic response that can account for shear-thinning in the suspension.

The equation for the Bingham model is given by:

\begin{align}
\tau < \tau_B, \dot{\gamma} &= 0 \\
\tau \geq \tau_B, \tau &= \tau_B + \mu_p \dot{\gamma}
\end{align}

(S1)

(S2)

The equation for the Herschel-Bulkley model is given by:

\begin{align}
\tau < \tau_y, \dot{\gamma} &= 0 \\
\tau \geq \tau_y, \tau &= \tau_y + K \gamma^n
\end{align}

(S3)

(S4)

For flow modeling, using the Bingham model makes for more tractable equations but if the material is shear-thinning, the Bingham model fit will tend to overestimate the yield stress. A compromise between simpler flow equations and good accuracy for fits can be made if we use a piecewise Bingham model over the range of shear rates of interest where we define a transition stress \(\tau_t\) above which we allow the yield stress and plastic viscosity to change while keeping the function piecewise continuous.

The equation for the piecewise Bingham model is given by

\begin{align}
\tau < \tau_B, \dot{\gamma} &= 0 \\
\tau \geq \tau_t, \tau &= \tau_t + \mu_p \dot{\gamma} \gamma^n
\end{align}

(S5)
\[ \tau \geq \tau_B, \tau = \tau_B + \mu_p \dot{\gamma} \]  \hspace{1cm} (S6)

\[ \tau \geq \tau_T, \tau = \tau_T' + \mu_p' \dot{\gamma} \]  \hspace{1cm} (S7)

For a shear-thinning material, the piecewise Bingham model will provide a more accurate fit than the Bingham model while keeping linear plastic terms for simpler flow equations. A kink at the transition stress is a consequence of this model as seen in Figure S3a.

**Multiple Gap Slip Correction for Parallel Plate Geometry**

If the rheometric steady shear flow curves show gap-dependence then the flow curves are not material properties and this gap-dependence is a signature of wall slip in the system. This can be corrected for using the following procedure from Yoshimura & Prud’homme\(^2\): for a given shear stress \(\tau\), the apparent shear rate \(\dot{\gamma}_a(\tau)\) can be kinematically decomposed by the following relation:

\[ \dot{\gamma}_a(\tau) = \dot{\gamma}(\tau) + \frac{2V_s(\tau)}{H} \]  \hspace{1cm} (S8)

where \(\dot{\gamma}(\tau)\) is the true shear rate experienced by the sample and \(V_s(\tau)\) is the slip velocity at each wall at the given stress. For each given stress, the apparent shear rate is plotted against \(1/H\) and a linear fit is applied to the curves. The intercept & the slope are used to extract the true shear rate and the slip velocity for the given stress respectively.

**Scaling of Mechanical Loss with GIFcell Size**
Here we analyze the mechanical energy consumed in operating the GIFcell as a function of its size. The mechanical energy per unit mass to tilt the cell by an angle $2\theta$ is given by:

$$e_{\text{mechanical}} = gL_{\text{travel}} \sin \theta$$  \hfill (S9)

where $L_{\text{travel}}$ is the length of the electrolyte chamber or “tank” as illustrated in Fig. 2c and $g$ is the gravitational force constant. As a starting point, consider that the mechanical energy for 25 flips of the prototype GIFcell is 0.032 J/g, which is in the order of $\sim10^{-4}$ of the electrochemical energy extracted for this system. The following table shows how the ratio of mechanical energy to electrochemical energy scales with tank length $L_{\text{tank}}$, assuming 25 tilt operations are needed to fully charge or discharge the cell.

**Table S1:** The effect of tank length $L_{\text{tank}}$ on the ratio of mechanical energy to electrochemical energy, assuming 25 tilt operations are needed to fully charge or discharge the cell.

<table>
<thead>
<tr>
<th>$L_{\text{tank}}$ (meters)</th>
<th>0.07 (lab scale)</th>
<th>0.1</th>
<th>1</th>
<th>10</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical to electrochemical energy ratio</td>
<td>0.023%</td>
<td>0.032%</td>
<td>0.32%</td>
<td>3.26%</td>
<td>32.6%</td>
</tr>
</tbody>
</table>

It is seen that a GIFcell could in principle be several meters long while retaining high mechanical efficiency. The other adjustable parameters are the energy density of the suspension, which could increase by a factor of 2 or 3 while remaining within the sulfur solubility limit, and the number of tilts required, which could decrease; both would further decrease the mechanical losses from those shown.
Figure S1: Comparing the slip-corrected flow curves measured at 25 °C of 0.5 vol% and 1.5 vol% KB of 2.5 M Li$_2$S$_8$ triglyme suspension (0.5 M LiTFSI salt and 1 wt% LiNO$_3$) with ketchup (Heinz 57®). All these fluids exhibit a yield stress and shear-thinning behavior.
**Figure S2:** (a) Comparison of fits to different yield stress models to the slip-corrected flow curve data measured for a 2.5 M Li$_2$S$_8$ suspension in triglyme with 0.5 vol% KB, 0.5 M LiTFSI and 1 wt% LiNO$_3$ at $T = 25^\circ$C. (b) Flow curves for a triglyme-based suspension at $T = 25$ °C measured at different gaps ($H = 1, 0.75, 0.5$ and $0.4$ mm) on a stainless steel and Teflon®.

**Figure S3:** A snapshot of Movie S2 shows how the droplet of 2.5 M Li$_2$S$_8$ suspension (0.5 vol% KB, 0.5 M LiTFSI and 1 wt% LiNO$_3$) behaves on (a) ABS-material and (b) Teflon®. The droplet spreads and sticks on to the surface in the former, while the same droplet rolls freely without getting pinned to the surface.
**Figure S4:** Comparing the advancing and receding contact angles of a 0 vol% and a 0.5 vol% KB, 2.5 M Li$_2$S$_8$ suspension (0.5 M LiTFSI and 1 wt% LiNO$_3$ in triglyme) on a clean Teflon® surface. The experiment was carried out using a goniometer (Ramé-hart model 590).
Figure S5: The current density extracted and the average speed of the catholyte show a dependence of the tilt angles (30°, 60° and 90°) of the GIFcell during potentiostatic discharge at 2.00 V. The dimensions of the flow channel are: $H = 1.6$ mm, $L = 80$ mm, $W = 13$ mm. The average speed of the suspension plug is calculated by dividing the length of flow ($L_{tank}$) with flow time. Catholyte: 2.5 M Li$_2$S$_8$ (with respect to the S) suspension with 0.5 vol% KB, 0.5 M LiTFSI, 1 wt% LiNO$_3$ in tetraglyme. Anode: Lithium metal.
**Figure S6:** 1\textsuperscript{st} and 5\textsuperscript{th} cycle of GIFcell angled at 10° (with respect to the horizontal) during electrochemical testing using potentiostatic mode of operation (Discharging at 2.05 V and charging at 2.6 V). Catholyte: 2.5 M Li\textsubscript{2}S\textsubscript{8} (with respect to the S) suspension with 0.5 vol% KB, 0.5 M LiTFSI, 1 wt% LiNO\textsubscript{3} in triglyme. Anode: Lithium metal.

**References**