# Electronic Supplementary Information

## A Low-Dissipation, Pumpless, Gravity Induced Flow Battery

Xinwei Chen[a, #], Brandon J. Hopkins[b, #], Ahmed Helal[b], Frank Y. Fan[a], Kyle C. Smith[a], Zheng Li[a], Alexander H. Slocum[b], Gareth H. McKinley[b], W. Craig Carter[a], Yet-Ming Chiang[a,*]

(a) Department of Materials Science and Engineering and (b) Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

***Corresponding author's e-mail: ychiang@mit.edu**

**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:

$$\tau < \tau_B, \dot{\gamma} = 0 \tag{S1}$$

$$\tau \geq \tau_B, \tau = \tau_B + \mu_p \dot{\gamma} \tag{S2}$$

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

$$\tau < \tau_y, \dot{\gamma} = 0 \tag{S3}$$

$$\tau \geq \tau_y, \tau = \tau_y + K\dot{\gamma}^n \tag{S4}$$

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

$$\tau < \tau_B, \dot{\gamma} = 0 \tag{S5}$$

$$\tau \geq \tau_B, \tau = \tau_B + \mu_p \dot{\gamma} \tag{S6}$$

$$\tau \geq \tau_t, \tau = \tau_B' + \mu_p' \dot{\gamma} \tag{S7}$$

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:

$$\dot{\gamma}_a(\tau) = \dot{\gamma}(\tau) + \frac{2V_s(\tau)}{H} \tag{S8}$$

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:

$$e_{mechanical} = gL_{travel}sin\theta \tag{S9}$$

where $L_{travel}$ 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 ~$10^{-4}$ 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 $L_{tank}$, assuming 25 tilt operations are needed to fully charge or discharge the cell.

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

| **$L_{tank}$ (meters)** | 0.07 (lab scale) | 0.1 | 1 | 10 | 100 |
|---|---|---|---|---|---|
| **Mechanical to electrochemical energy ratio** | 0.023% | 0.032% | 0.32% | 3.26% | 32.6% |

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.

**Supplementary Figures**

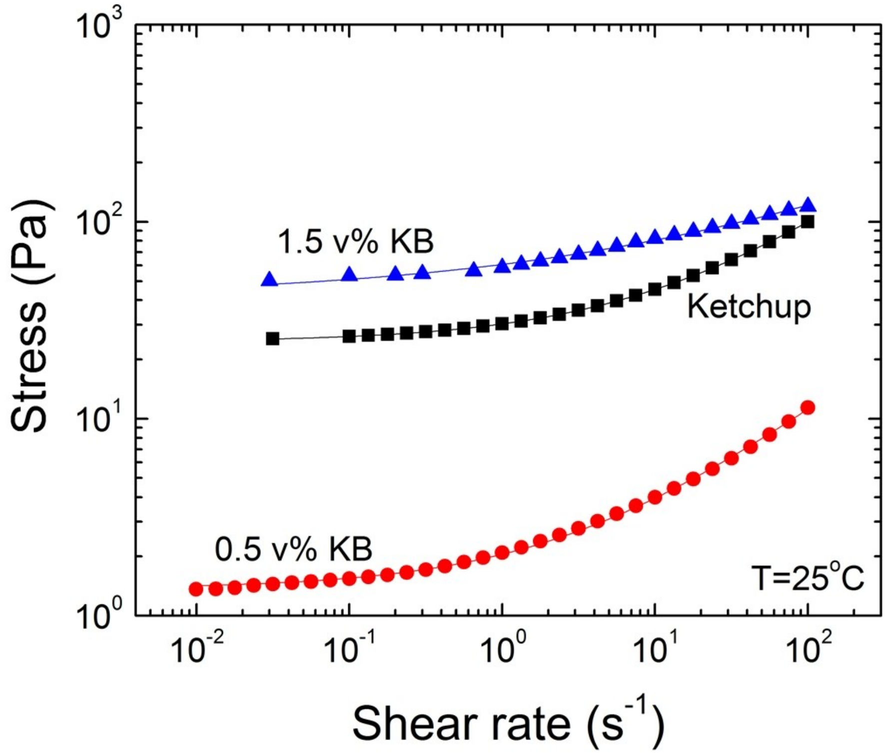


**Figure S1:** Comparing the slip-corrected flow curves measured at 25 °C of 0.5 vol% and 1.5 vol% KB of 2.5 M $Li_2S_8$ triglyme suspension (0.5 M LiTFSI salt and 1 wt% $LiNO_3$) with ketchup (Heinz 57®). All these fluids exhibit a yield stress and shear-thinning behavior.

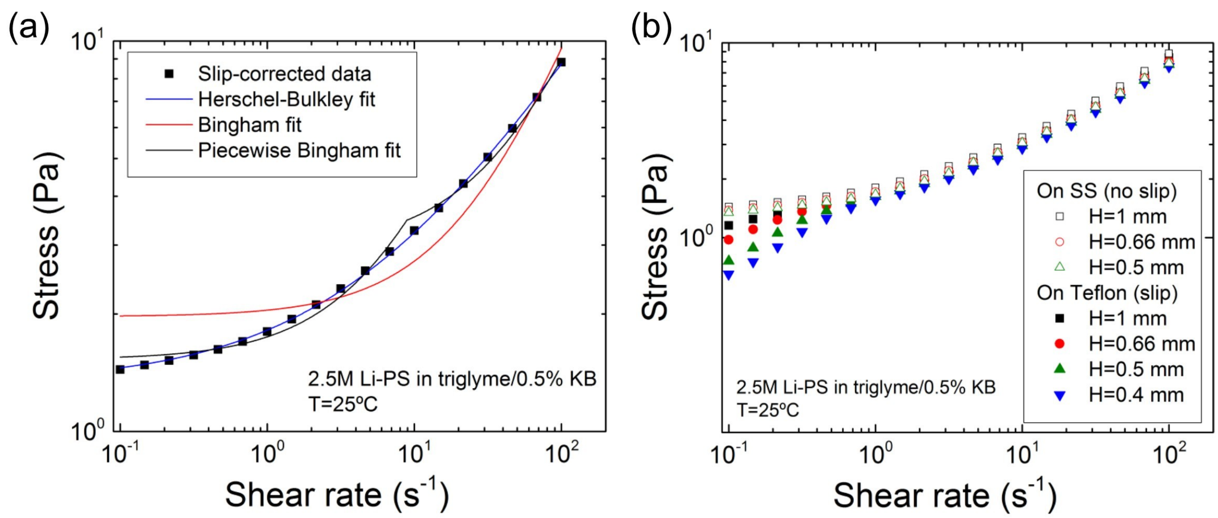


**Figure S2:** (a) Comparison of fits to different yield stress models to the slip-corrected flow curve data measured for a 2.5 M $Li_2S_8$ suspension in triglyme with 0.5 vol% KB, 0.5 M LiTFSI and 1 wt% $LiNO_3$ at $T = 25$°C. (b) Flow curves for a triglyme-based suspension at $T = 25$ °C measured at different gaps ($H$ = 1, 0.75, 0.5 and 0.4 mm) on a stainless steel and Teflon®.

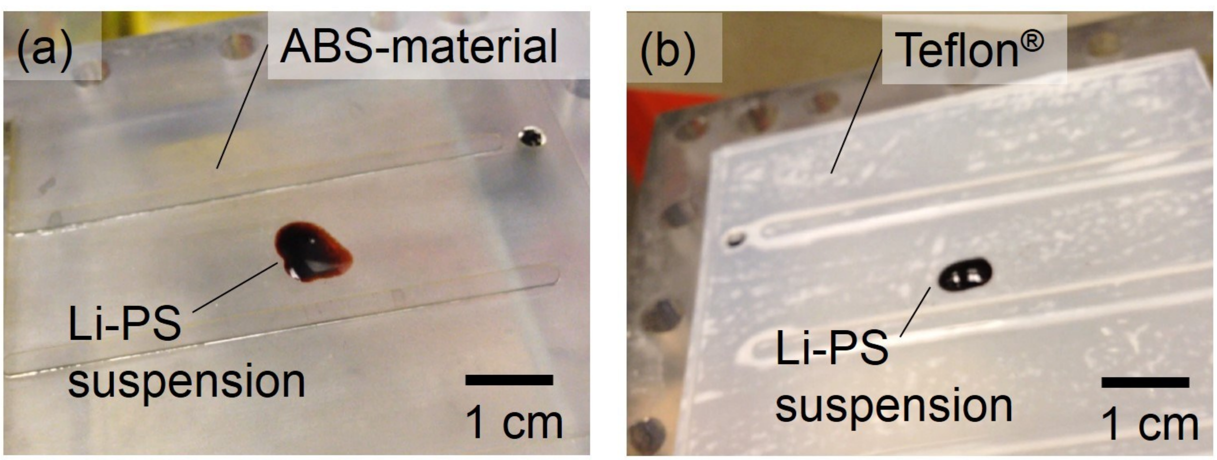


**Figure S3:** A snapshot of Movie S2 shows how the droplet of 2.5 M $Li_2S_8$ suspension (0.5 vol% KB, 0.5 M LiTFSI and 1 wt% $LiNO_3$) behaves on (a) ABS-material and (b) Teflon®. The droplet spreads and sticks on to the surface in the former, while the same droplet rolls freely without getting pinned to the surface.

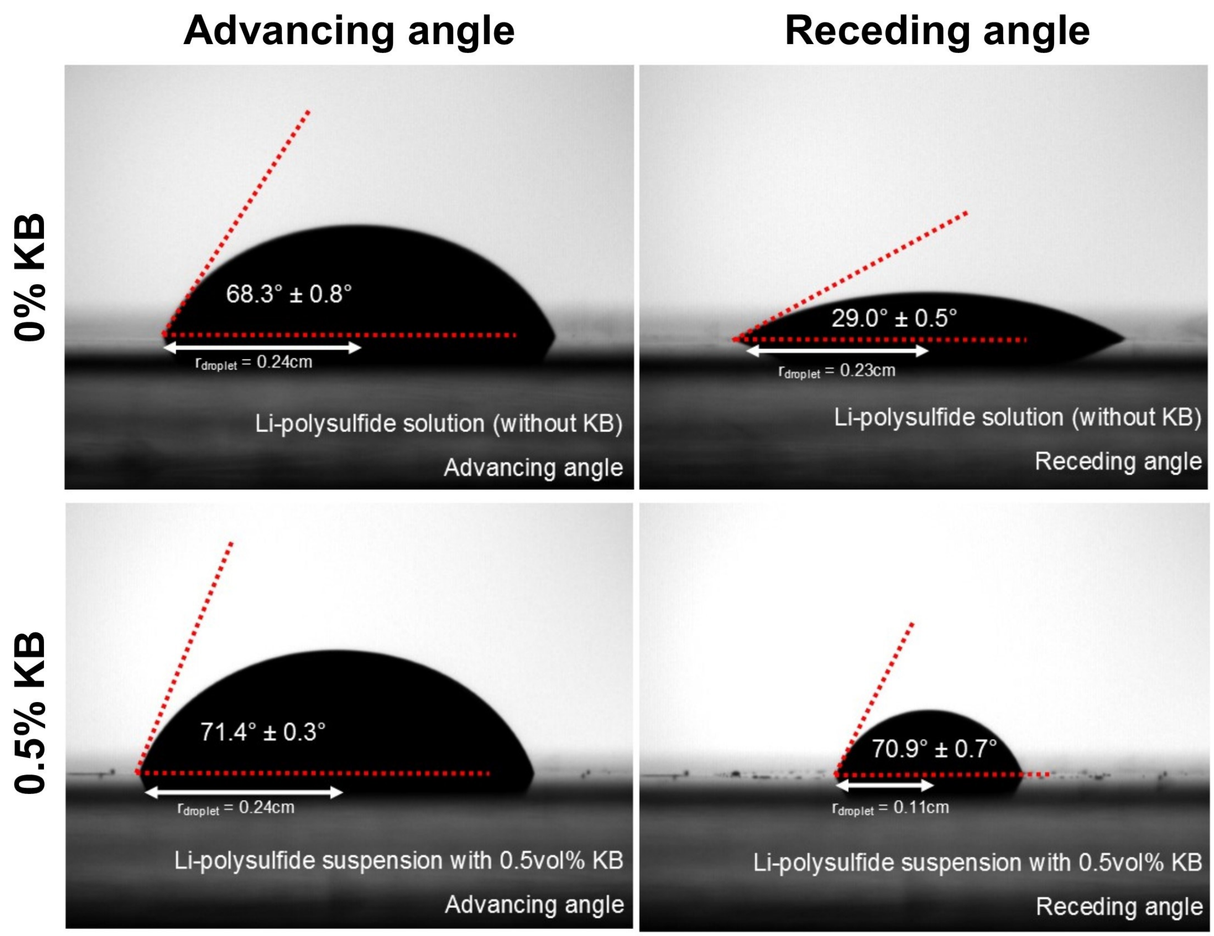


**Figure S4:** Comparing the advancing and receding contact angles of a 0 vol% and a 0.5 vol% KB, 2.5 M $Li_2S_8$ suspension (0.5 M LiTFSI and 1 wt% $LiNO_3$ in triglyme) on a clean Teflon® surface. The experiment was carried out using a goniometer (Ramé-hart model 590).

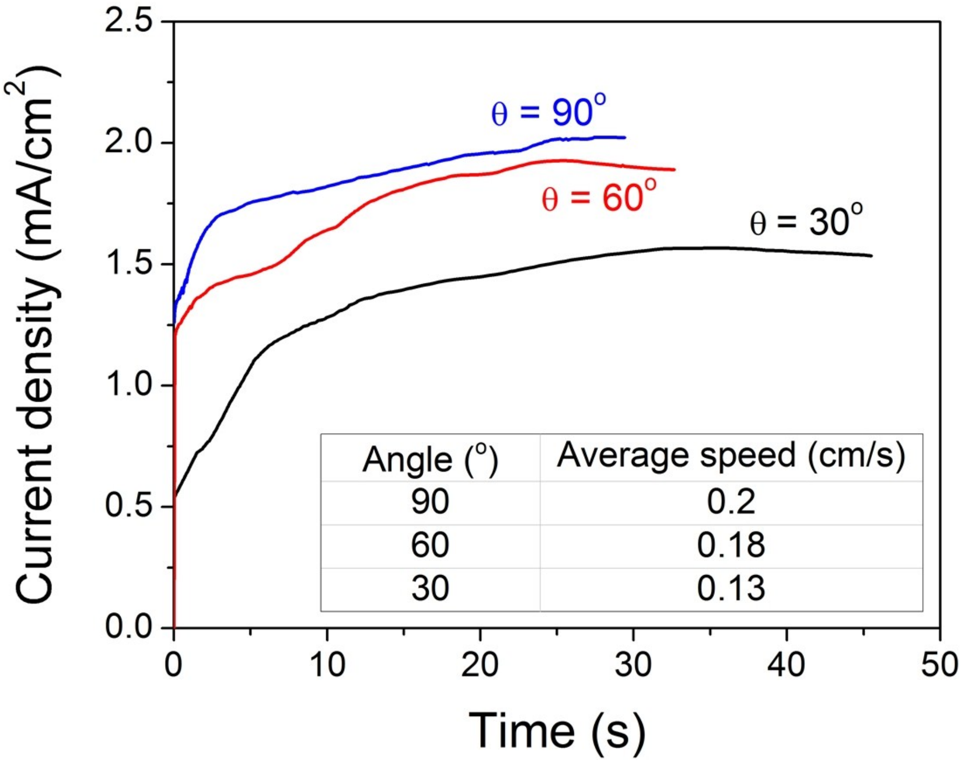


**Figure S5:** The current density extracted and the average speed of the catholyte show a dependence of the tilt angles (30°, 60° and 90°) of the GIFcell during potentiostatic discharge at 2.00 V. The dimensions of the flow channel are: $H$ = 1.6 mm, $L$ = 80 mm, $W$ = 13 mm. The average speed of the suspension plug is calculated by dividing the length of flow ($L_{tank}$) with flow time. Catholyte: 2.5 M $Li_2S_8$ (with respect to the S) suspension with 0.5 vol% KB, 0.5 M LiTFSI, 1 wt% $LiNO_3$ in tetraglyme. Anode: Lithium metal.

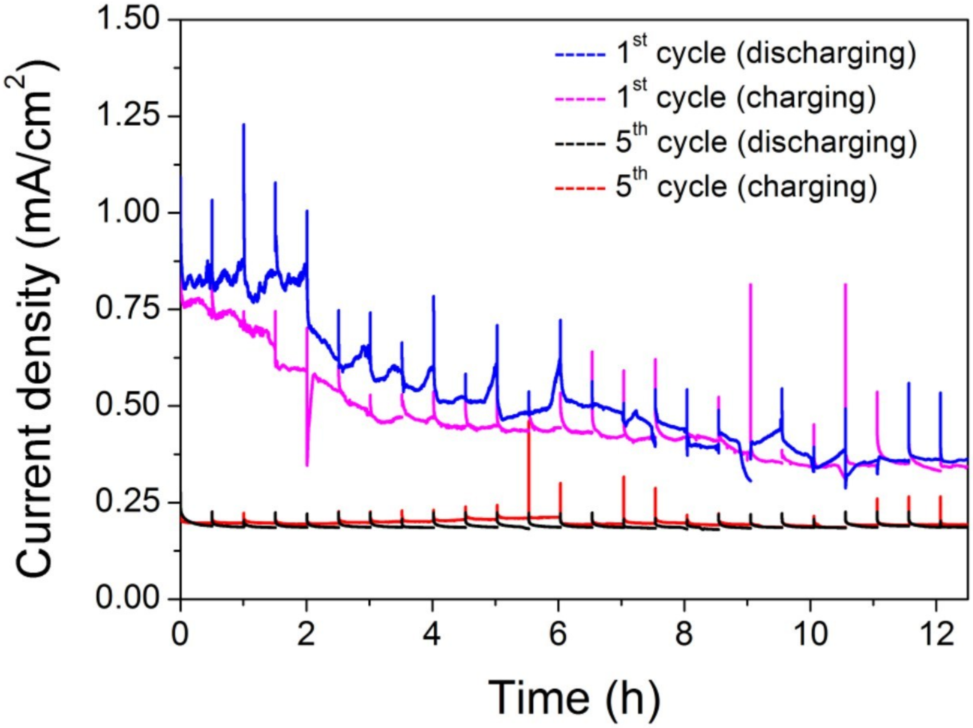


**Figure S6:** 1st and 5th cycle of GIFcell angled at 10° (with respect to the horizontal) during electrochemical testing using potentiostatic mode of operation (Discharging at 2.05 V and charging at 2.6 V). Catholyte: 2.5 M $Li_2S_8$ (with respect to the S) suspension with 0.5 vol% KB, 0.5 M LiTFSI, 1 wt% $LiNO_3$ in triglyme. Anode: Lithium metal.

## References

1. H. A. Barnes, *J. Nonnewton. Fluid Mech.*, 1999, **81**, 133–178.

2. A. Yoshimura and R. K. Prud'homme, *J. Rheol.*, 1988, **32**, 53–67.