Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Solar rechargeable redox flow battery based on Li_2WO_4/LiI couples in dual-phase electrolytes

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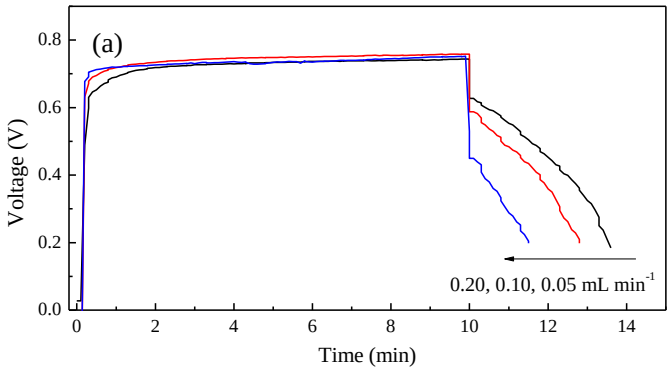
Fabrication of the cell. The cell was consisted of the dye-sensitized TiO_2 photo-anode, anode/electrolyte, cathode/electrolyte, and LISICON lithium-ion-conducting glass ceramic (LICGC, 0.15 mm-thick, $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ from OHARA Inc., Japan) membrane. Silicone membrane gasket was used to fix membrane and Pt coated Ti mesh. Pt coated Ti mesh (2 cm × 2 cm) was used as working electrode in anode and cathode compartments. The TiO_2 photo-anode was fabricated by doctor-blading a commercial TiO_2 sol (Solaronix, Ti-Nanoxide T/SP) onto the FTO glass and sintered for 30 min at 450 °C in muffle furnace (heating rate of 10°C min^{-1}). The TiO_2 electrode was immersed in dye (N719, 5.0×10^{-4} M in ethanol solution) at room temperature for 24 h in dark, then rinsed with ethanol and dried. The effective cell area was 4 cm^2.

Performance measurement. Cyclic voltammetry (CV) of the LiI (0.01 M LiI/0.1M $LiClO_4$ in propylene carbonate) and Li_2WO_4 (0.01M Li_2WO_4/0.1M $LiClO_4$ in H_2O) was carried out to identify redox potential and electrochemical reversibility using an IM6ex electrochemical workstation (Zahner IM6ex). CV was conducted by using a conventional three-electrode system with the scan rate of 50 mV s^{-1}. Pt-coated Ti mesh was used as working electrode, Pt/FTO as a counter electrode, and Ag/Ag^+ in acetonitrile or saturated calomel electrode (SCE) as the reference electrode. CV of the dye (N719) adsorbed onto FTO (10^{-4} M N719 in ethanol) was carried out in 0.1 M $LiClO_4$ in anhydrous acetonitrile at the scan rate of 1 V s^{-1}. In the solar rechargeable flow battery, Li_2WO_4 was used as anode (0.1M Li_2WO_4 and 0.2M $LiClO_4$ in H_2O), and LiI was used as cathode (0.1M LiI and 0.5M TBP in propylene carbonate). The electrolyte was 1.2 mL in volume, which was re-circulated in each half compartment by two miniature peristaltic pumps. When CV and cell performance are measured, $LiClO_4$ is added as the supporting electrolyte salt to insure the stable ionic conductivity of the aqueous electrolyte. After soaking in electrolyte for 15 min, the cell was illuminated by a solar simulator (CHF-XM500, Beijing Trusttech) under 100 mW cm^{-2} irradiation and calibrated by a standard silicon solar cell. The galvanostatic method was employed to measure the electrochemical capacity and cycle life of the battery at room temperature using a LAND-CT2001A instrument.



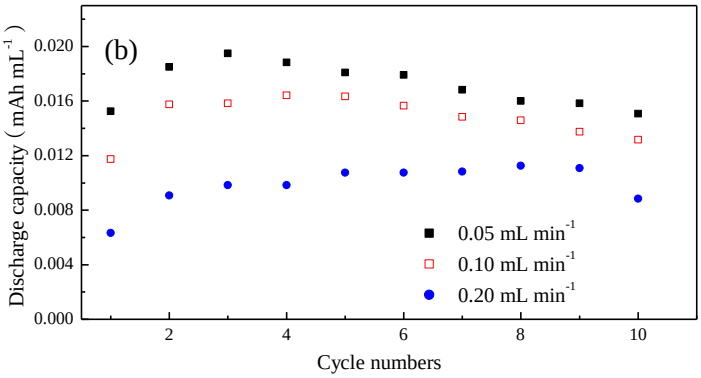


Fig. S1 (a) Potential profiles of the solar rechargeable redox flow battery at photo-charge under 100 mW cm^{-2} irradiation for 10 min and the current density of 0.075 mA cm^{-2} for discharging with different flow rates. (b) Discharge capacities vs. cycle number during 10 cycles with different flow rates.

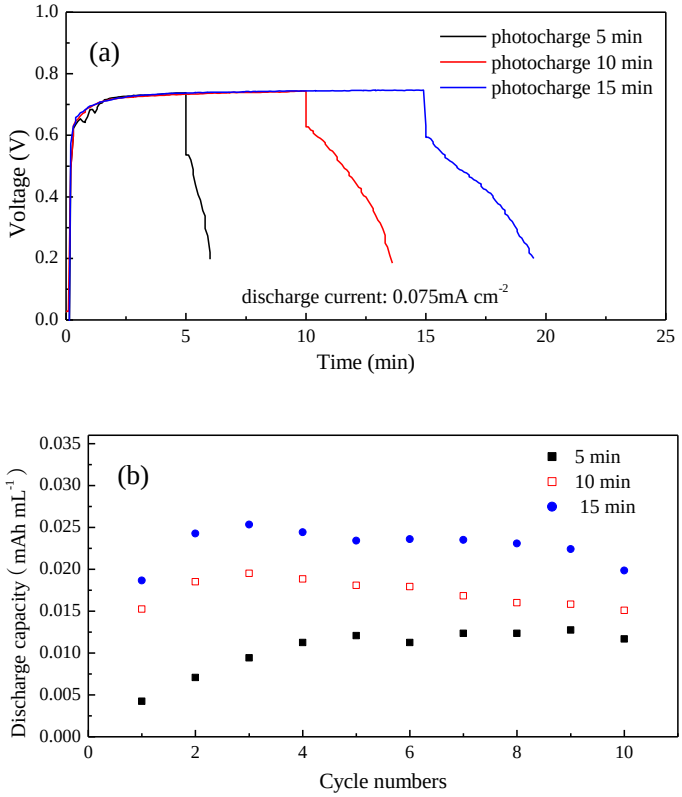


Fig. S2. (a) Potential profiles of the solar rechargeable redox flow battery at photo-charge under 100 mW cm^{-2} irradiation for different times, and the current density of 0.075 mA cm^{-2} for discharging with the flow rate of 0.05 mL min^{-1}. (b) Discharge capacities vs. cycle number during 10 cycles for different photo-charge times.