Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Using Waste Li ion batteries as Cathodes in Rechargeable Li-Liquid Batteries

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Chemicals

Carbon black (Vulcan XC-72), used as a conductive additive to the liquid cathodes, was purchased from FuelCellStore. For the surface modification of carbon black, 6N hydrochloric acid was purchased from Fisher Scientific. Both Sodium nitrate ($NaNO_2$, ACS reagent, ≥ 97.0%) and sulfanilic acid (4-aminobenzenesulfonic acid, ACS reagent, 99%) were purchased from Sigma-Aldrich. As for the liquid cathode substance used, TIMREX K56 Graphite was purchased from TIMCAL. And for the organic electrolyte, 1M $LiPF_6$ in ethylene carbonate (EC): diethyl carbonate (DEC) (1:1 volume ratio) was purchased from Novolyte Corp. The $LiFePO_4$ used as a cathode, and the graphite (mesocarbon microbeads) and $Li_4Ti_5O_{12}$ powder, each used as active anode materials, were all purchased from MTI Corporation. Used for anode composites in this study, SUPER P carbon black, as conductive additives, and polytetrafluoroethylene (PTFE, G-580, ICI), as binder, were purchased from TIMCAL. In fabrication of the multi-layer electrochemical cell, the Li ion conducting glass ceramic plate, $Li_{1+x+y}Ti_{2-x}Al_xP_{3-y}Si_yO_{12}$ (LTAP), used as the solid electrolyte, measuring 1 inch × 1 inch in area, 150 μm thick, and with a $\sigma_{Li} \approx 10^{-4}$ S/cm at room temperature, was

purchased from OHARA Inc. And finally, the carbon paper used as the current collector was purchased from FuelCellStore.

Surface modification of carbon black (Vulcan XC-72)

We adopted azo-coupling of sulfanilic acid using *in situ* generated diazonium cations to provide hydrophilic properties to the surface of the carbon.[1] First, 300 mg of Vulcan XC-72 were dispersed in 50 ml of 0.5 M HCl solution. After adding 0.525 g of sulfanilic acid, the solution was vigorously stirred for 30 min. Once the reaction completed, 0.41 g of $NaNO_2$ was added and stirred for 24 hours in order for the mixture to fully mix. Finally, the surface modified Vulcan XC-72 was obtained via vacuum filtration, followed by washing with DI water, and then drying for 24 h at room temperature.

Preparation of the liquid cathode

Surface modified Vulcan XC-72 (0.05 g) was transferred into a small vial, and then, 3 g of 1M $LiPF_6$ in EC:DEC, 0.5 g of $LiFePO_4$, 0.05 g of graphite, and 12 g of DI water, respectively, were added to the vial. This vial was placed in Ultrasonic cleaner B1510-MT for one hour under ultrasonication. After sonication, approximately 1.5 mL of solution was used for each experiment. The pH of the as-synthesized liquid cathode was 6.20 (slightly acidic due to the presence of the sulfonic group on the surface of Vulcan XC-72).

Fabrication of the multi-layer electrochemical cell

The LTAP solid electrolyte was placed on the aluminum laminate pouch with a hole in the center and then fixed with epoxy. The epoxy was again applied to bond that pouch to the anode side of the cell, and then completely dried for several hours. The graphite coated onto

the copper foil as the anode was welded onto the stainless steel rod. On the other hands, the $Li_4Ti_5O_{12}$ electrode was spread over the stainless mesh, which was welded onto the stainless steel rod. The electrode composition of the graphite was 80:10:10 (graphite : Super P : PTFE weight ratio), while that of $Li_4Ti_5O_{12}$ was 70:20:10 ($Li_4Ti_5O_{12}$: Super P : PTFE weight ratio). The active mass loading of graphite and $Li_4Ti_5O_{12}$ were 7.5 mg cm^{-2} and 5.3 mg cm^{-2}, respectively. Once either one of the anodes were placed on the stainless steel rod, the anode side of the cell was then assembled. While inside a glove box, the organic electrolyte was injected into the cell through the holes in the anode side of cell. The carbon paper used as the current collector was inserted in the cathode side before assembling the cell. After fabrication of the cell, the liquid cathode was injected through the holes in the cathode compartment. The holes in the anode and cathode were blocked to minimize any decomposition or contamination of either the organic electrolyte or the liquid cathode. The charge & discharge voltages were measured by Solartron 1470E.

1 M. Weissmann, S. Baranton, J. M. Clacens, and C. Coutanceau, *Carbon*, 2010, **48**, 2755-2764.