Electronic Supplementary Information

In-situ formed polymer gel electrolytes for lithium batteries with inherent thermal shutdown safety features

Hongyao Zhou, Haodong Liu, Yejing Li, Xiujun Yue, Xuefeng Wang, Matthew Gonzalez, Ying Shirley Meng, and Ping Liu*

Department of Nanoengineering, University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093, United States

E-mail: piliu@eng.ucsd.edu

Experimental

Preparation of $Li_4Ti_5O_{12}$ (LTO) cathode: LTO powder (Nanomyte B-10 supplied from NEI, U.S.) was mixed with polyvinylidene difluoride (PVDF) and carbon black (Super P) in a weight ratio of 80:10:10. The loading density of LTO was 0.9 mg cm^{-2}. For the thermal shutdown test, LTO, polyvinyl alcohol (PVA) and Super P were mixed in a weight ratio of 70:15:15 to enhance the wettability of the gel electrolyte. The loading density of LTO was 2.1 mg cm^{-2}.

Gel Permeation Chromatography (GPC): GPC system consist of: a pump (Shimadzu, Japan); 2 in-line 5 μm size-exclusion columns (10^3 and 10^4 Å, Phenogel, Phenomenex, U.S.) within a column oven (Shimadzu); and a RID-10A differential refractive index detector (Shimadzu). The mobile phase consists of 0.1% LiBr in DMF at a flow rate of 1 mL/min and 50 °C. The sample injection volume was 25 μL. Peaks were calibrated against a set of polystyrene standards.

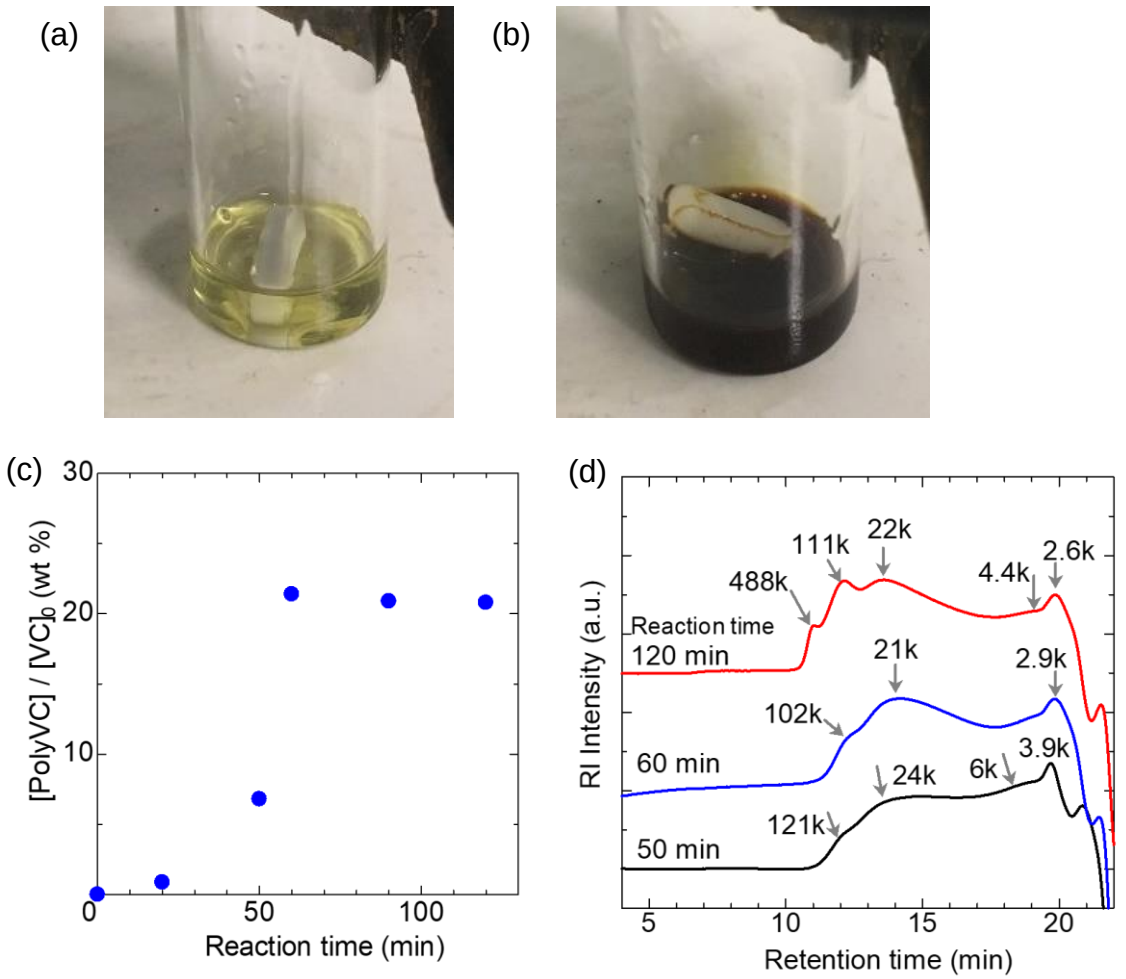

Figure S1. Photograph of VC-LiI (1 mol kg^{-1}) solution before heating (a) and after heating (b) at 80 ℃. (c) Weight ratio of polyVC to the initial amount of VC ($[VC]_0$ = 2 g) monomer after varied reaction time (T = 80 ℃). The polymer gel after 60 minutes of reaction is used as the electrolyte in the experiment, and the weight ratio of polyVC to solvent VC in the gel electrolyte is 1:4. (d) Reflective index (RI) intensity vs retention time of polyVC after 50 min, 60 min and 120 min of the reaction. Number-averaged molecular weight (M_n) of the polymer at each peak is labeled in the figure. The polyVC synthesized with LiI shows a broad distribution of the M_n.

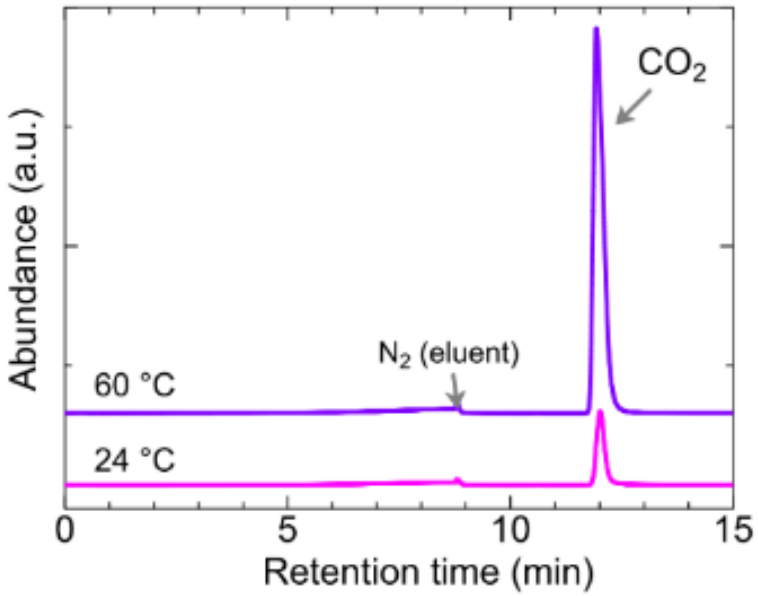

Figure S2. Gas chromatography of the gas generated during the polymerization of VC by LiI at 24 and 60 ℃.

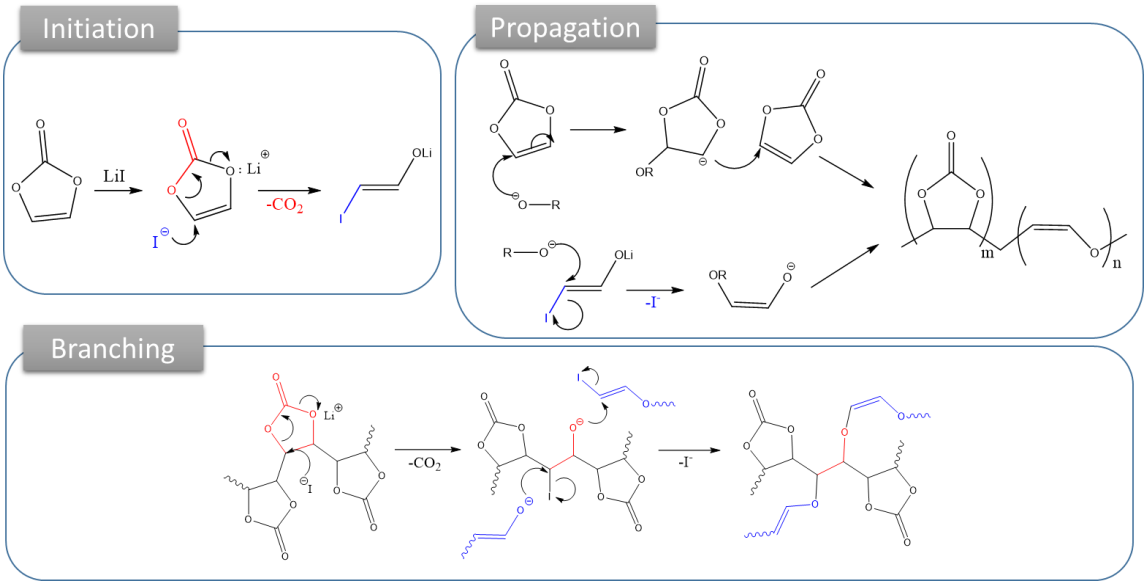

Figure S3. Initiation, propagation, and branching reactions of polyVC which is polymerized from VC and LiI.

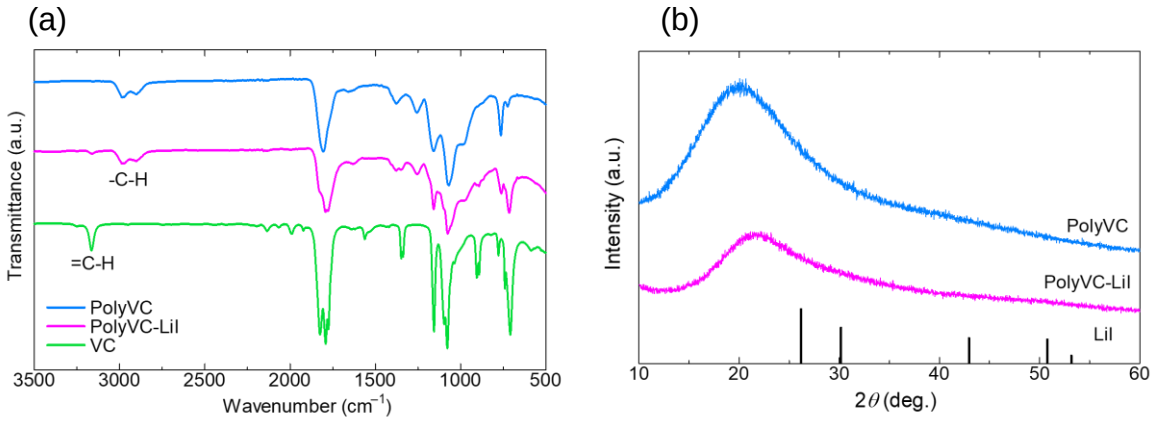

Figure S4. (a) IR spectrum of solidified polyVC-LiI gel electrolyte after five months of storage under Ar atmosphere, and the spectrum after removal of LiI. (b) Powder X-ray diffraction pattern of solidified polyVC-LiI electrolyte before (PolyVC-LiI)/after (PolyVC) removal of LiI. No LiI peaks are visible in the polymer gel. Diffraction pattern of LiI is cited from Inorganic Crystal Structure Database (ICSD) 414244.

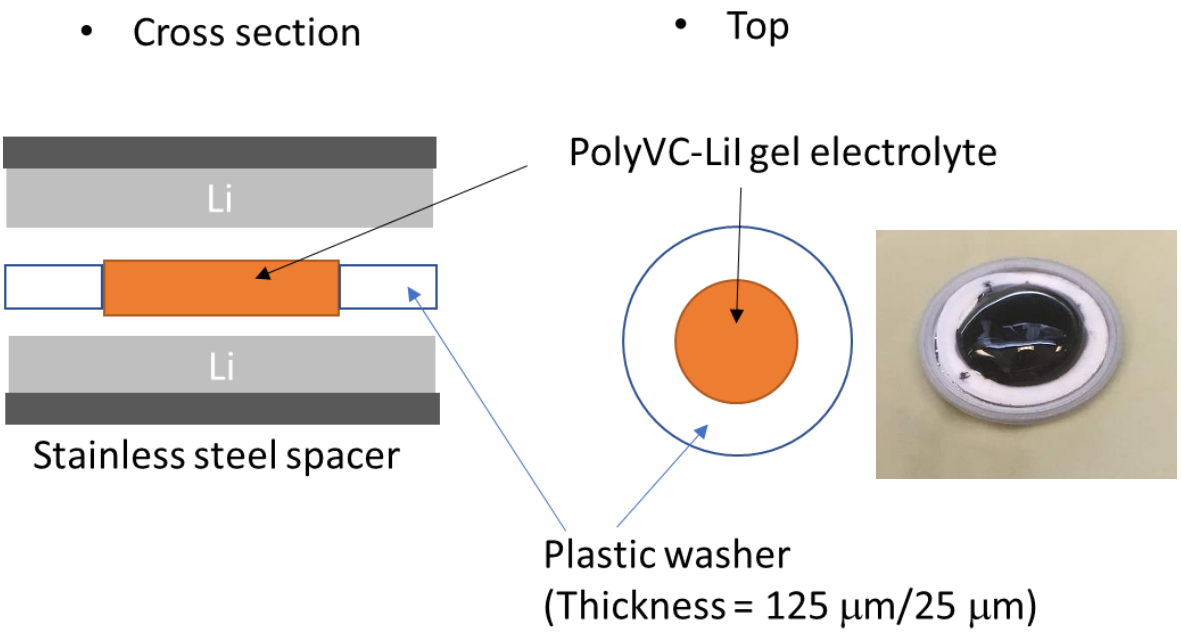

Figure S5. Cross section and top view of Li//Li symmetric cell. The two electrodes are separated by a plastic washer with a thickness of 125 μm and 25 μm (PTFE for 125 μm, PE for 25 μm). The inner diameter of the washer is 12 mm. The cell is crimped into CR2016 coin cell case.

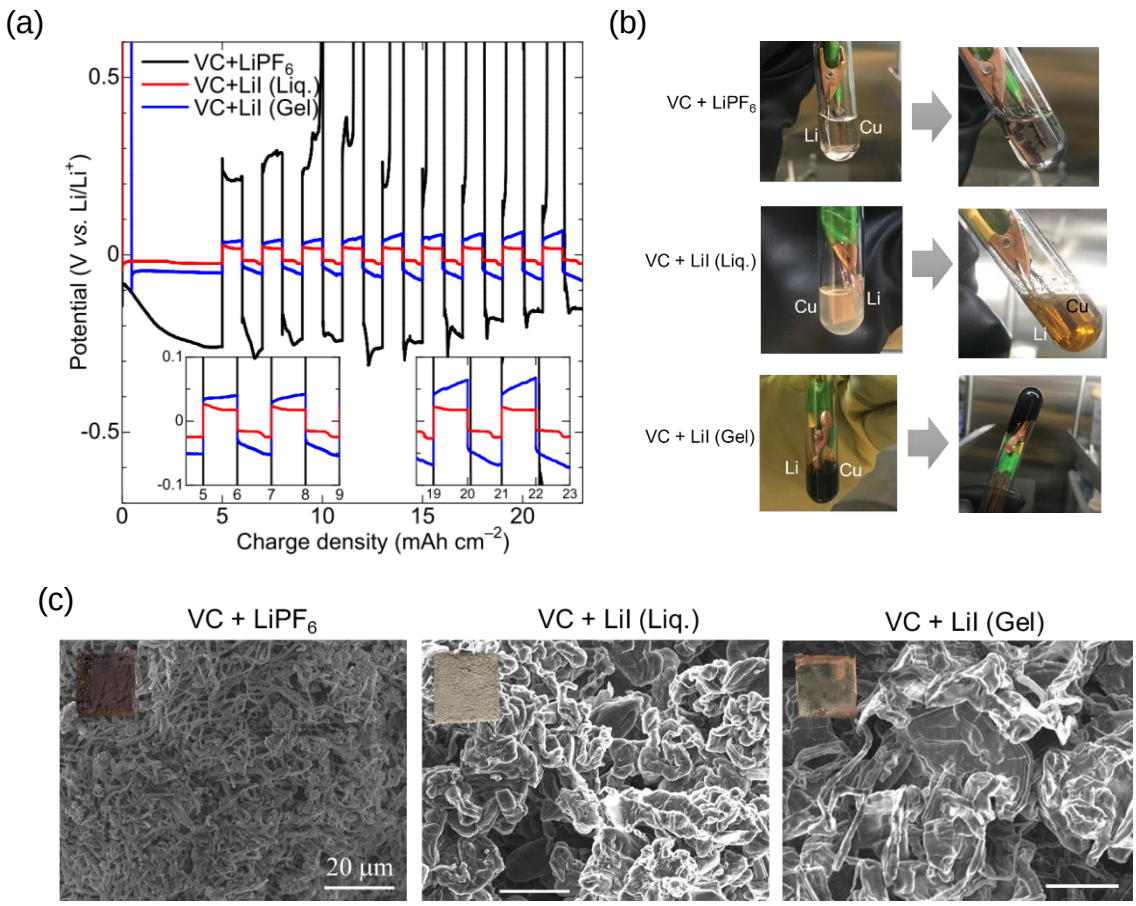

Figure S6. (a) Potential profile of Li//Li symmetric cycling in a test tube flooded with various VC-based electrolytes: VC + 1 mol kg^{-1} $LiPF_6$; VC + 1 mol kg^{-1} LiI at liquid state; VC + 1 mol kg^{-1} LiI at gel state. 5 mAh cm^{-2} of Li was deposited on Cu foil and 1 mAh cm^{-2} of Li was stripped/deposited repeatedly for 9 cycles. (b) Photo images of the state of the electrolytes before (left column) and after (right column) Li//Li cycling. (c) SEM images of the deposited Li metal on Cu foil. Scale bar = 20 μm. The inset shows the photo image of the electrodeposited Li on Cu electrode.

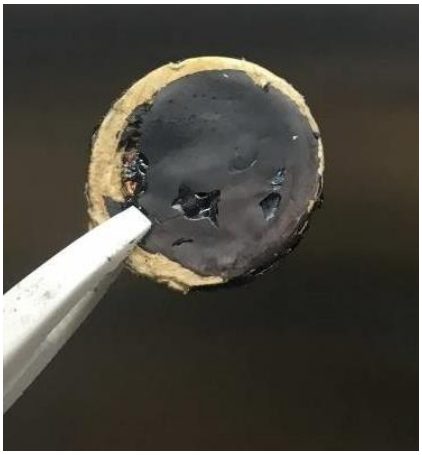

Figure S7. VC-based polyVC-LiI gel electrolyte after heating at 80 °C. The gel was completely solidified and covered the surface of Li metal.