

Supporting Information

Designing boron-based single-ion gel polymer electrolytes for lithium batteries by photopolymerization

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Experimental – Synthesis of lithium borate methacrylic monomers

Chemicals. — 2-Hydroxyethyl methacrylate (HEMA, 97%, Aldrich), Borane tetrahydrofuran complex solution 1.0 M in THF (BH₃, Aldrich), 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, ≥99%, Aldrich), and n-Butyllithium 2.5M solution in hexanes, (nBuLi, ACROS) were used as received. Triethylene glycol monomethyl ether (TEG, 95%, Aldrich) was distilled at the rotary evaporator at 70°C and reduced pressure. The hexane solvent (SharpLab) was dried with anhydrous MgSO₄ before use. BH₃-THF and n-Butyl lithium are very highly moisture-sensitive reagents so they need to be handled under inert atmosphere in all steps.

Lithium butyl(2-((bis((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)boryl)oxy)ethyl methacrylate) (SIM-FF).

2-Hydroxyethyl methacrylate (10 mmol, 1.3 g) and 30 ml of dry hexane were charged into the 100 ml two-neck flask, the solution was stirred with argon flow and subsequently cooled in an acetone-liquid N₂ bath, avoiding solidification of the system. BH₃-THF complex solution 1M in THF (10 mmol, 10 ml) was carefully taken on a sealed syringe and added "dropwise", while H₂ was expelled from the system with nitrogen flow. Then, the reaction mixture was slowly warmed to room temperature and stirred for 30 min more. Subsequently, the system was cooled again in an acetone/liquid N₂ bath and, 1,1,1,3,3,3-Hexafluoro-2-propanol (20 mmol, 4 ml) was added dropwise. Afterward, the system was again heated to RT for 1 hour to ensure the second evolution of H₂ was ended. Then the system was again cooled in an acetone-liquid N₂ bath and, carefully, n-Butyl lithium 2.5 M in hexane (10 mmol, 4 ml) was added under an inert atmosphere. A viscous transparent liquid was formed, which was stirred at room temperature for another 2 hours. Finally, the product was precipitated and washed with cold diethyl ether. The obtained transparent liquid was

placed in a vial and dried in a vacuum line at 40°C for 24h. Yield: 4.62 g (87%); Found: ¹H NMR (400 MHz, D₂O): δ (ppm) = 6.02 (s, 1H, CH₂=C(CH₃)–), 5.51 (t, 1H, CH₂=C(CH₃)–), 4.38 (sp, 2H, B-O-CH(CF₃)₂); 4.19 (t, 2H, CO-O-CH₂), 3.86 (t, 2H, CO-O-CH₂-CH₂-O-B), 1.85 (s, 3H, CH₂-C(CH₃)); 1.39 (q, 4H, B-CH₂-CH₂-); 1.23 (sx, 4H, B-CH₂-CH₂-); 1.03 (c, 4H, (CH₂)₂-CH₃); 0.78 (t, 12H, B-CH₂); ¹¹B NMR (400 MHz, D₂O): δ (ppm) = 8.2 (s, -CH₂-B-(OR)₂); ¹⁹F NMR (400 MHz, D₂O): δ (ppm) = -78.2 (s, CF₃).

Lithium butyl(2-((bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)boryl)oxy)ethyl methacrylate) (SIM-GG).

2-Hydroxyethyl methacrylate (10 mmol, 1.3 g) and 30 ml of dry hexane were charged into the 100 ml two-neck flask, the solution was stirred with argon flow and subsequently cooled in an acetone-liquid N₂ bath, avoiding solidification of the system. BH₃-THF complex solution 1M in THF (10 mmol, 10 ml) was carefully taken on a sealed syring and added "dropwise", while H₂ was expelled from the system with nitrogen flow. Then, the reaction mixture was slowly warmed to room temperature and stirred for 30 min more. Subsequently, the system was cooled again in an acetone/liquid N₂ bath and triethylene glycol monomethyl ether (20 mmol, 4 ml) was added dropwise. The system was again heated to RT. for 1 hour to ensure the second evolution of H₂ was ended. Afterward, the system was cooled again in an acetone-liquid N₂ bath and carefully, n-Butyl lithium 2.5 M in hexane (10 mmol, 4 ml) was added under an inert atmosphere. A viscous transparent liquid was formed, which was stirred at room temperature for another 2 hours. Finally, the product was precipitated and washed with cold diethyl ether. The obtained transparent liquid was placed in a vial and dried in a vacuum line at 40°C for 24h. Yield: 4.45 g (85%); Found: ¹H NMR (400 MHz, D₂O): δ (ppm) = 6.02 (s, 1H, CH₂=C(CH₃)–), 5.51 (t, 1H, CH₂=C(CH₃)–), 4.19 (t, 2H, CO-O-CH₂), 3.86 (t, 2H, BO-CH₂-CH₂-COO), 3.80-3.46 (m, 24H, O-CH₂-CH₂-O);

3.31 (s, 6H, CO-CH₃); 1.85 (s, 3H, CH₂-C(CH₃)); 1.35 (q, 4H, B-CH₂-CH₂-); 1.28 (sx, 4H, B-CH₂-CH₂-); 0.21 (c, 4H, (CH₂)₂-CH₃); 0.74 (t, 12H, B-CH₂); ¹¹B NMR (400 MHz, D₂O): δ (ppm) = 8.2 (s, -CH₂-B-(OR)₂).

Lithium butyl(2-((2-((1,1,1,3,3,3-hexafluoropropan-2-yl (2-(2-(2-methoxyethoxy)ethoxy) ethyl) boryl)oxy)ethyl methacrylate) (SIM-FG).

2-Hydroxyethyl methacrylate (10 mmol, 1.3 g) and 30 ml of dry hexane were charged into the 100 ml two-neck flask, the solution was stirred with argon flow and subsequently cooled in an acetone-liquid N₂ bath, avoiding solidification of the system. BH₃-THF complex solution 1M in THF (10 mmol, 10 ml) was carefully taken on a sealed syringe and added "dropwise", while H₂ was expelled from the system with nitrogen flow. Then the reaction mixture was slowly warmed to room temperature and stirred for 30 min more. Subsequently, the system was cooled again in an acetone/liquid N₂ bath, and triethylene glycol monomethyl ether (10 mmol, 4 ml) was added dropwise. The system was again heated to RT for 1 hour to ensure the second evolution of H₂ was ended. Then the system was cooled again in an acetone/liquid N₂ bath and 1,1,1,3,3,3-Hexafluoro-2-propanol (10 mmol, 4 ml) was added dropwise. Afterwardsthe system was again heated to RT. for 1 hour to ensure the third evolution of H₂ has ended. Then the system was again cooled in an acetone-liquid N₂ bath and, carefully, n-BuLi 2.5 M in hexane (10 mmol, 4 ml) was added under an inert atmosphere. A viscous transparent liquid was formed, which was stirred at room temperature for another 2 hours. Finally, the product was precipitated and washed with cold diethyl ether. The obtained transparent liquid was placed in a vial and dried in a vacuum line at 40°C for 24h. Yield: 4.85 g (0.92%); Found: ¹H NMR (400 MHz, D₂O): δ (ppm) = 6.02 (s, 1H, CH₂=C(CH₃)-), 5.51 (t, 1H, CH₂=C(CH₃)-), 4.38 (sp, 1H, B-O-CH(CF₃)₂); 4.19 (t, 2H, CO-O-CH₂), 3.86 (t, 2H, BO-CH₂-CH₂-COO), 3.80-3.46 (m, 12H, O-CH₂-

$\text{CH}_2\text{-O}$); 3.31 (s, 6H, CO-CH_3); 1.85 (s, 3H, $\text{CH}_2\text{-C}(\text{CH}_3)$); 1.35 (q, 4H, $\text{B-CH}_2\text{-CH}_2\text{-}$); 1.28 (sx, 4H, $\text{B-CH}_2\text{-CH}_2\text{-}$); 0.21 (c, 4H, $(\text{CH}_2)_2\text{-CH}_3$); 0.74 (t, 12H, B-CH_2); ^{11}B NMR (400 MHz, D_2O): δ (ppm) = 8.2 (s, $\text{-CH}_2\text{-B}(\text{OR})_2$); ^{19}F NMR (400 MHz, D_2O): δ (ppm) = -78.2 (s, CF_3).

Table S1. SIGPE electrolytes compositions in wt%.

Name	SIM-xx ^{a)}	PEGDM ^{b)}	G4 ^{c)}
SIPE-FG-60G4	20	20	60
SIPE-FG-30G4	60	10	30
SIPE-FG	95	5	Solvent free
SIPE-FF-60G4	20	20	60
SIPE-FF-30G4	60	10	30
SIPE-FF	95	5	Solvent free
SIPE-GG-60G4	20	20	60
SIPE-GG-30G4	60	10	30
SIPE-GG	95	5	Solvent free

^{a)} SIM-FG; SIM-FF or SIM-FG; ^{b)} Poly(ethylene glycol) dimethacrylate; ^{c)} Tetraethylene glycol dimethyl ether (tetraglyme).

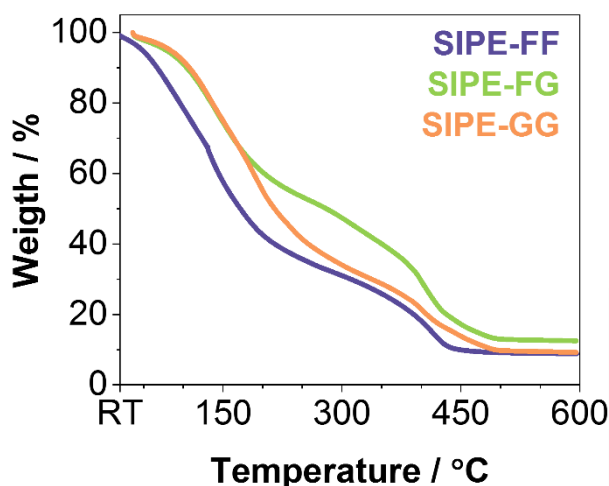


Figure S1. TGA curve of solvent-free polymer electrolytes (SIPE-FF, SIPE-FG, and SIPE-GG) undertaken under nitrogen atmosphere and $10\text{ °C}\cdot\text{min}^{-1}$.

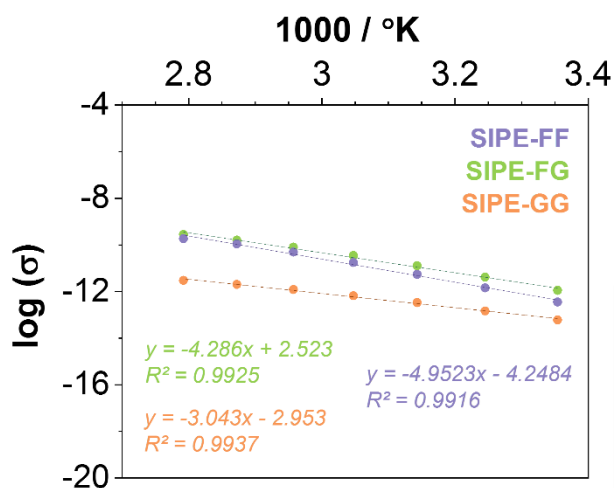


Figure S2. Arrhenius fitting plot for SIPE-FF, SIPE-FG, and SIPE-GG electrolytes (solvent-free).

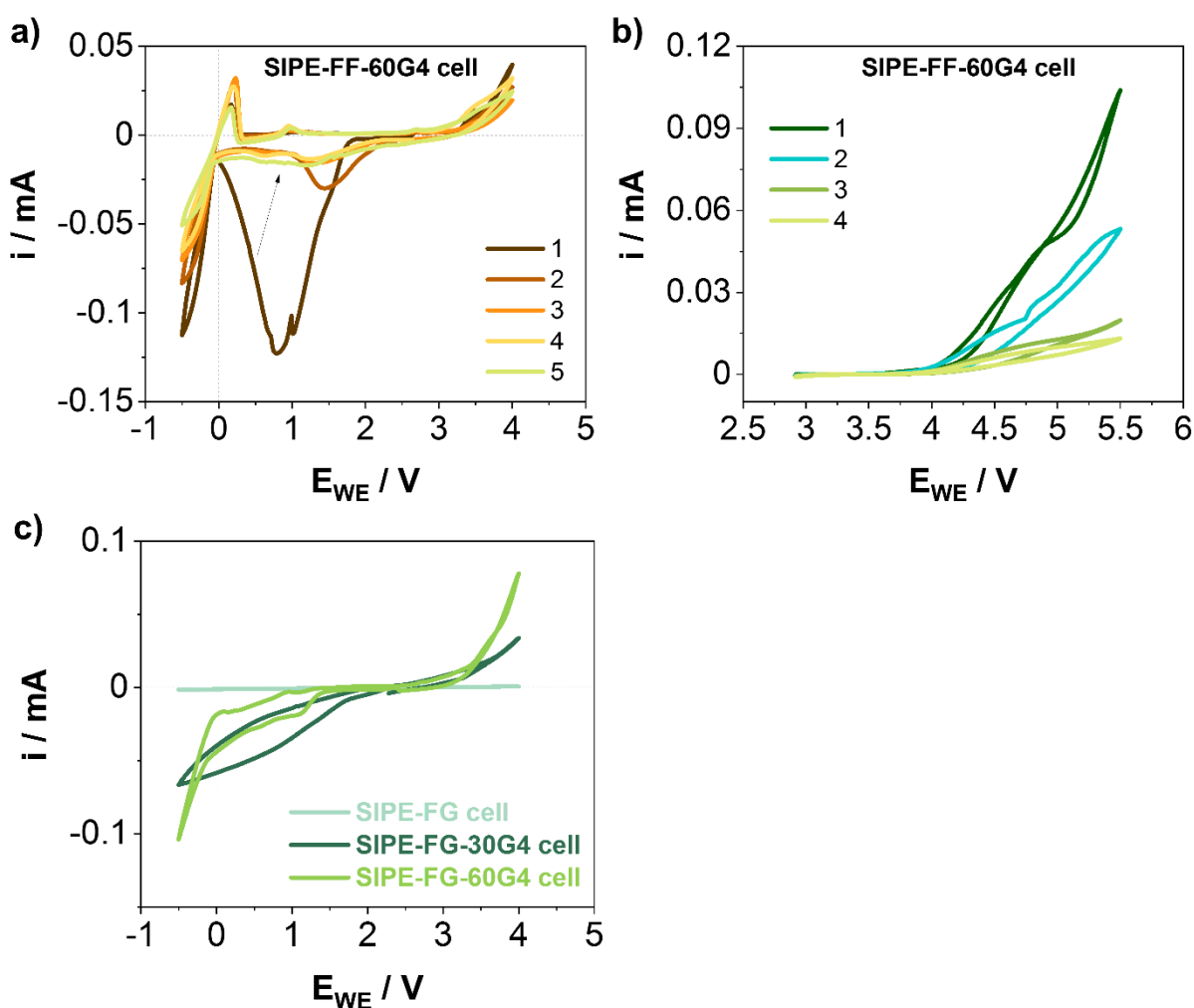


Figure S3. Voltammograms at a scan rate of $0.2 \text{ mV} \cdot \text{s}^{-1}$: a) Li/SIPE-FF-60G4/Cu cell, first 5 cycles are plotted; b) Li/SIPE-FF-60G4/SS cell, first 4 cycles are plotted; and c) Li/Electrolyte/Cu cells of SIPE-FG-x electrolytes family.

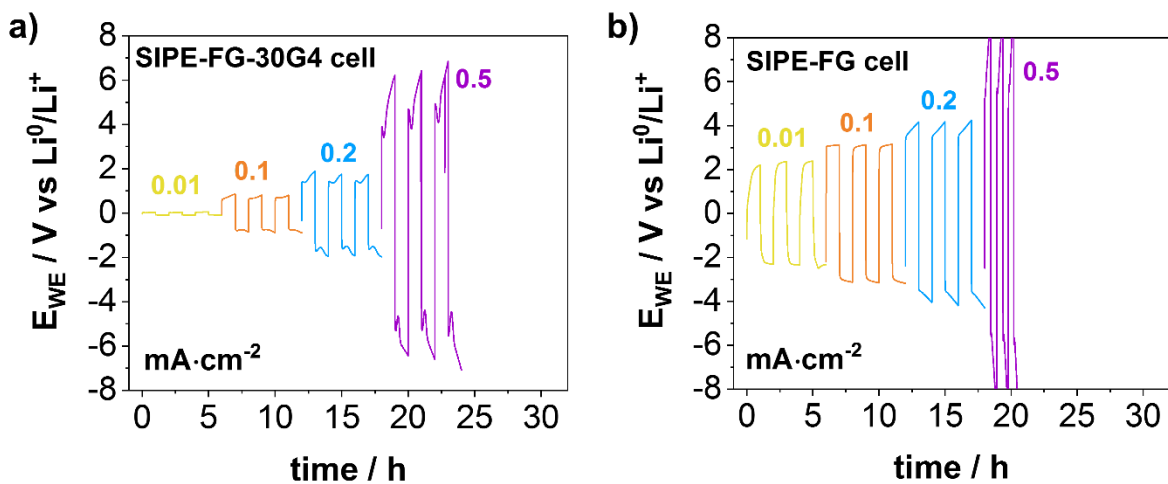


Figure S4. Lithium stripping/plating curves at increasing current densities from 0.01 to 0.5 $\text{mA}\cdot\text{cm}^{-2}$ in symmetrical lithium cells: a) SIPE-FG-30G4 cell and b) SIPE-FG cell.