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ARTICLE TYPE

Electrodeposition of Germanium from Supercritical Fluids

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Additional figures

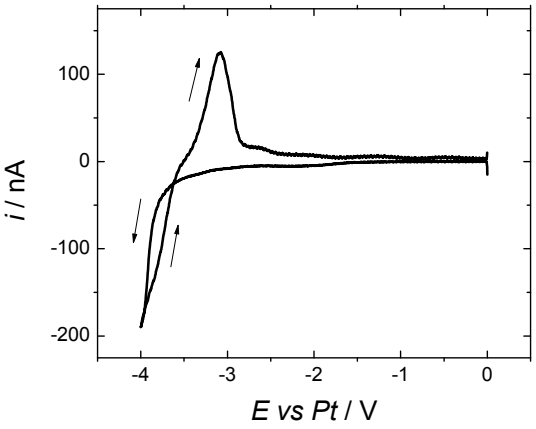

Fig. S1. Cyclic voltammetry of 8.16 mM Li[B{3,5-$(CF_3)_2C_6H_3$}$_4$] in CH_3CN. *T* 294 K. Working electrode 25 µm diameter Pt disc, counter electrode Pt grid, reference electrode 0.5 mm Pt disc. Arrows indicate sweep direction. Sweep rate 500 mV s^{-1}.

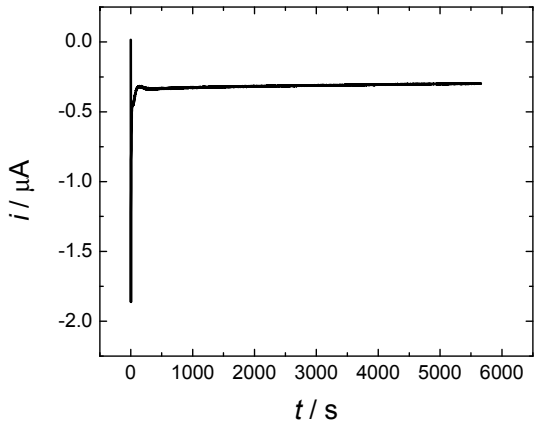

Fig. S3. Chronoamperometry at 0.5 mm diameter platinum disc electrode (shown in Fig. 3b). 7.1 mM [NBu^n_4][$GeCl_3$] in $scCO_2$ with 12.1 wt % CH_3CN and 30 mM [NBu^n_4][BF_4], at 310 K and 17.2 MPa. Counter electrode Pt grid, reference electrode 0.5 mm Pt disc. Potentials 0 V (2 s) and -1.4 V (5656 s). Charge passed = 1.78 mC.

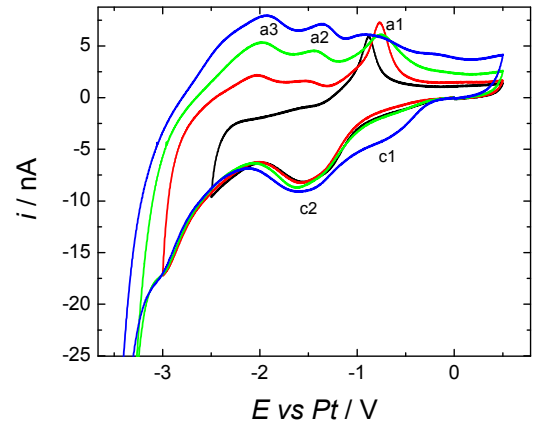

Fig. S2. Cyclic voltammetry of 5 mM [NBu^n_4][$GeCl_3$] in 20 mM Li[B{3,5-$(CF_3)_2C_6H_3$}$_4$] in CH_3CN, at *T* 298 K. Working electrode 25 µm diameter Pt disc, counter electrode Pt grid, reference electrode 0.5 mm Pt disc Sweep rate 500 mV s^{-1}.

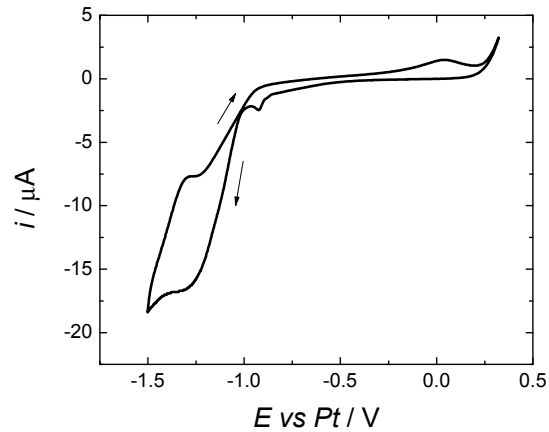

Fig. S4. Cyclic voltammetry of 5 mM [NBu^n_4][$GeCl_3$] in $scCO_2$ with 12.1 wt % CH_3CN and 20 mM Li[B{3,5-$(CF_3)_2C_6H_3$}$_4$], at 310 K and 17.2 MPa. Working electrode 0.5 mm diameter Pt disc, counter electrode Pt grid, and reference electrode 0.5 mm Pt disc. Sweep rate = 100 mV s^{-1}.

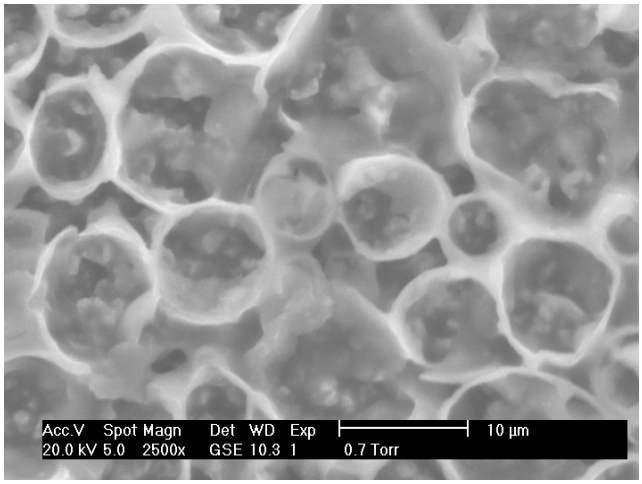

Fig. S5. SEM of film on 0.5 mm diameter Au disc electrode after chronoamperometry in 5 mM $[NBu^n_4][GeCl_3]$ in $scCO_2$ with 12.1 wt % CH_3CN and 20 mM $Li[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$, at 310 K and 17.2 MPa.. Counter electrode Pt grid, reference electrode 0.5 mm Pt. Potentials applied 0 V (2 s) and -2 V (2300 s).

Experimental

$GeBr_2$ was obtained from Aldrich and used as received. $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$, $Li[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$, and $[NBu^n_4][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ were made by modified literature procedures as described previously.[1]

$[Li(12\text{-crown-}4)][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$: $Li[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ (0.435 g, 0.5 mmol) (prepared using $LiBF_4$ in place of $NaBF_4$)[2] and 12-crown-4 (0.09 g, 0.05 mmol) were dissolved separately in CH_2Cl_2 (5 mL) and then combined. The clear, colourless solution was stirred for 10 min and then the solvent was removed and the resulting white solid was dried *in vacuo* and used for electrochemical studies. The product was handled in a dry N_2-purged glove box.

The preparations of $[GeF_4\{Me_2N(CH_2)_2NMe_2\}]$,[3] $[GeF_4(MeCN)_2]$,[4] and $[Ge(12\text{-crown-}4)][CF_3SO_3]_2$ [5,6] have been described previously.

$[GeCl_2(4,4'\text{-didecyl-}2,2'\text{-bipyridine})]$: 4,4'-Didecyl-2,2'-bipy[7] (0.08 g, 0.50 mmol) was added to a solution of $[GeCl_2(1,4\text{-dioxane})]$ (0.218 g, 0.50 mmol) in CH_2Cl_2 (5 mL) at room temperature with stirring. After 1 h the solvent was removed *in vacuo* to leave a white solid which was washed with petroleum ether and dried *in vacuo*. Yield: 0.13 g, 90%. IR (Nujol) cm^{-1}: 256(s), 242(sh) Ge–Cl. ^1H NMR ($CDCl_3$): 0.81 (t, [3H]), 1.20–1.41(m, [14H], 1.73 (m, [2H]), 2.91 (t, [2H]), 7.67 (d, [H]), 8.33 (s, [H]), 8.82 (d, [H]).

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