

# Alkali Reduction of Graphene Oxide in Molten Halide Salts: Production of Corrugated Graphene Derivatives for High-Performance Supercapacitors

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## Control experiments:

### Reduction with molten lithium:

Lithium powder and GO were mixed and charged into an alumina crucible in a glovebox. The alumina crucible was placed at the bottom of alumina reactor similar to the one described in the experimental section. The reactor was then purged flushed with Ar gas for 4 hours prior to being heated to 220 °C in order to melt the Lithium. The mixture was then allowed to cool under Ar atmosphere for X mins/hours. The GO was collected from the top of the solidified sample then washed and dried using the method described in the experimental section.

### Reduction with lithium vapor:

Graphene oxide was suspended from the top and lithium rods were placed at the bottom of an air-tight stainless steel vessel filled with Ar gas (see figure S1). The vessel was then heated to 250 °C using a vertical furnace for the required time. After cooling, the GO samples were collected and washed using the same procedure in the experimental section.

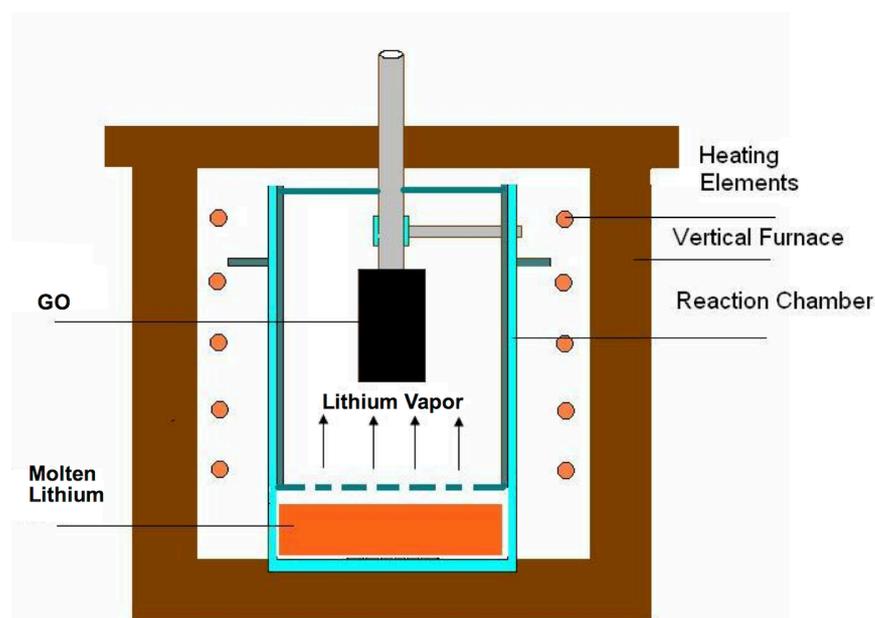


Figure S1: the reaction apparatus used for the GO reduction with Li vapor.

## Calculating the specific capacitance obtained from CV and charge-discharge curves

From charge-discharge measurements, the specific capacitances of the rGO were obtained from the acquired data using following equation:

$$C = 4I\Delta t / m\Delta V$$

Where  $C$  represents the specific capacitances,  $I$  the constant charge current,  $\Delta t$  for the discharging period,  $m$  for the mass of graphene used as electrodes,  $\Delta V$  for the voltage of capacitor after constant current charging.

From CV curves, the specific capacitances were calculated according to the following equation:

$$C = (\int IdV) / (vmV)$$

where  $I$  represents the current density during charging-discharging,  $V$  is the potential,  $v$  is the potential scanning rate, and  $m$  is the mass of the graphene electrodes.

## Times required for GO reduction by different methods reported in literature.

Process	Time required	C/O Ratio	I <sub>D</sub> /I <sub>G</sub> Raman
Reduction in pure hydrazine. <sup>1</sup>	One week	10.3	>1
Reduction in three steps with sodium borohydride at 80 °C, aryl diazonium salt and hydrazine. <sup>2</sup>	27 h	N/P	N/P
Reduction with alcohol. <sup>3</sup>	24 h	7	>1
Reduction in hydrazine solution at 100 °C. <sup>4</sup>	24 h	10.3	>1
Reduction of GO- Polystyrene composite with dimethylhydrazine at 80 °C. <sup>5</sup>	24 h	N/P	N/P
Reduction with hydrazine vapor at 40 °C and subsequently anneal at 400 °C. <sup>4,6</sup>	22 h	N/P	N/P
Reduction with hydroquinone. <sup>7</sup>	20 h		>2
Thermal reduction under vacuum at 1100 °C. <sup>6</sup>	6 h	N/P	N/P
Reduction with Fe powder. <sup>8</sup>	6 h	7.9	0.32
Hydrothermal reduction at 180 °C. <sup>9</sup>	6 h	5.7	0.9
Reduction with sodium borohydride solution. <sup>10</sup>	2 h (thin film)	8.6	>1
Reduction with hydrazine vapour. <sup>11</sup>	3.5h (thin film)	N/P	N/P
Reduction with Hydrazine vapor at low pressure. <sup>12</sup>	72h	7.3	N/P
Reduction with hydrobromic acid at 110 °C <sup>13</sup>	24	3.9	0.89
Reduction with urea at 95 °C. <sup>14</sup>	30	4.5	N/P
Hydrothermal reduction with sodium ascorbate at 95 °C. <sup>15</sup>	1.5	10.3	>1
<b>Reduction with Li in molten LiCl-KCl at 370 °C (Present Work)</b>	<b>8</b>	<b>7</b>	<b>0.22</b>
<b>Reduction with Ca in molten CaCl<sub>2</sub> at 900 °C (Present Work)</b>	<b>2</b>	<b>14.5</b>	<b>0.18</b>
<b>Reduction with Li in molten CaCl<sub>2</sub> at 700 °C (Present Work)</b>	<b>4</b>	<b>10.4</b>	<b>0.20</b>

Although some processes in the literature was reported to take shorter time than the alkaline metal reduction in molten halides flux, healing graphene and recovering its graphenic properties as can be detected from the low I<sub>D</sub>/I<sub>G</sub> ratio and the re-appearance of the 2D band in the Raman spectra is a clear advantage of the alkaline metal reduction.

**Carbon to oxygen ratio for the GO reduced without molten salt flux.**

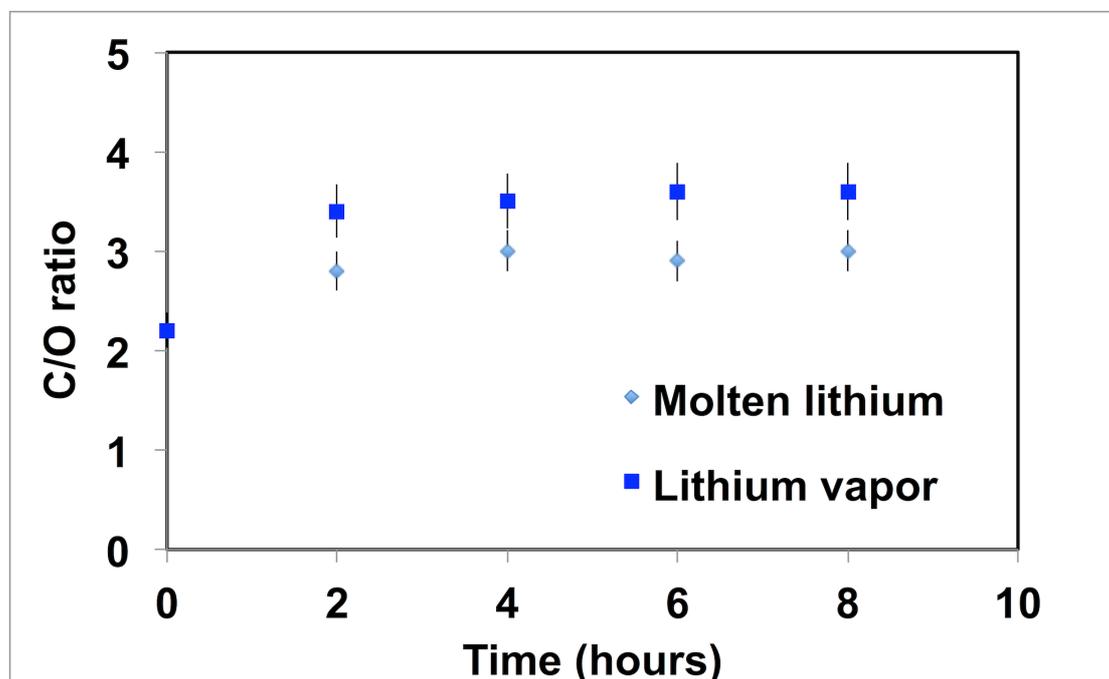


Figure S2: the carbon to oxygen ratio calculated using the XPS analysis for the graphene oxide after reduction with molten Li and Li vapor. Formation of LiOH on the top of the molten Li layer prevented further reduction.

## Effect of the Capacitance of the Ni Foam current collector

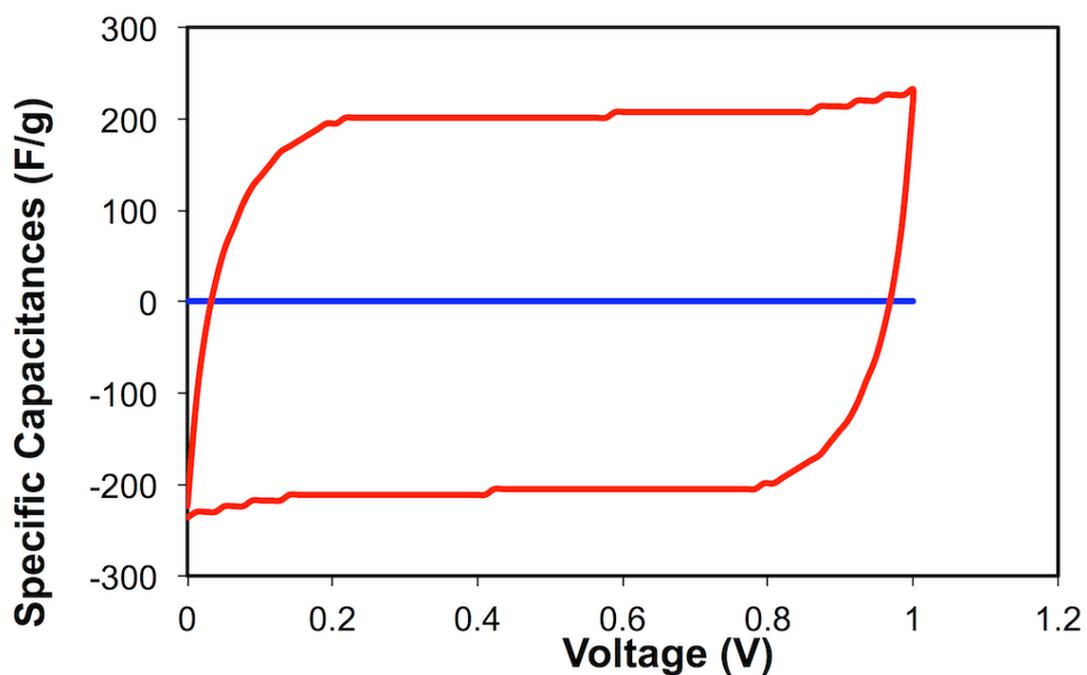


Figure S3: the specific capacitance obtained from the Ni foam current collector (blue) as compared with that obtained from the rGO porous electrode (red). The measurements were conducted using 6 M KOH solution as described in the experimental section.

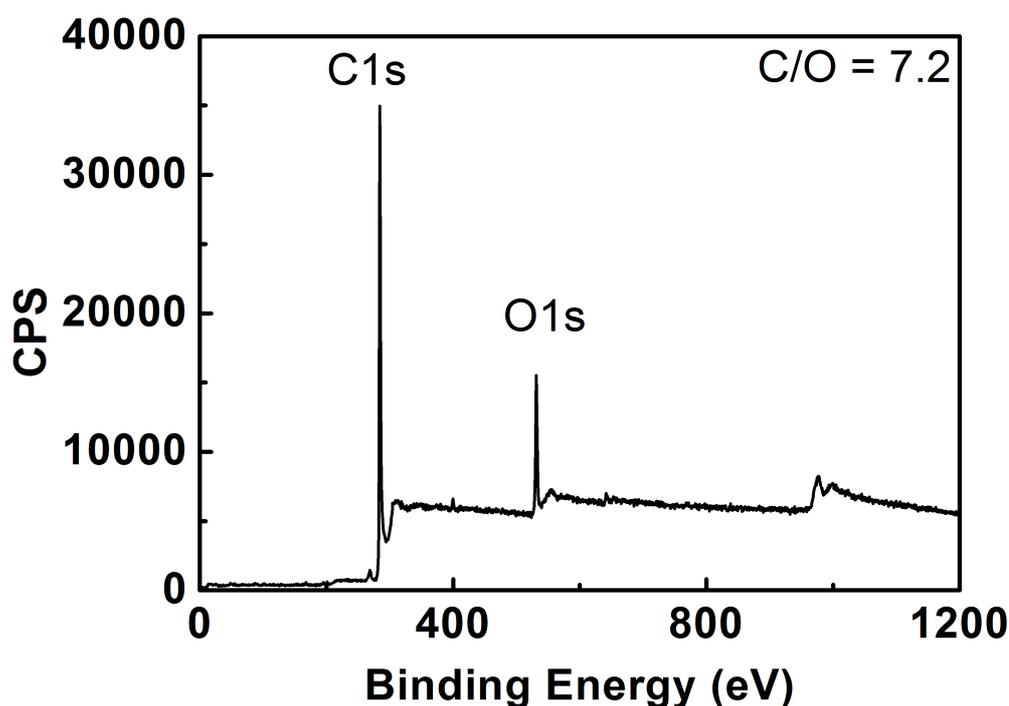


Figure S4: Wide scan XPS for the reduced GO in Li-LiCl-KCl molten salts at 370 °C. The absence of any peaks except those of oxygen and carbon clearly indicates there is no residue from the reducing agent or from the molten salts flux

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