

**A Series of substituted propylene carbonate (PC) –  
an investigation of graphite exfoliation**  
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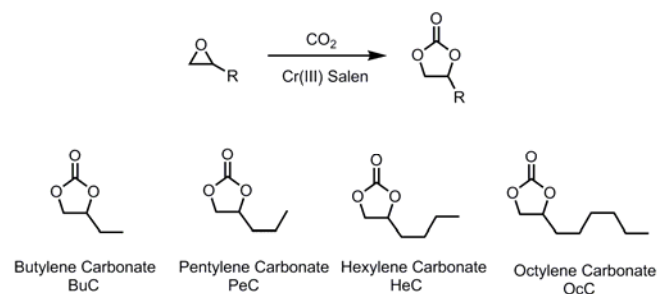
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### Introduction

A series of cyclic carbonate derivatives with different alkyl substitutes are synthesized and studied as solvents for graphite electrode based lithium ion half cells. It shows that when the alkyl chain length is short such as butylene carbonate (two carbons) and pentylene carbonate (three carbons), graphite exfoliation occurs, which is similar to that of PC solvents. Cyclic carbonate with long alkyl chains length such as hexylene carbonate (four carbons) and octylene carbonate (six carbons) are able to prevent graphite exfoliation.

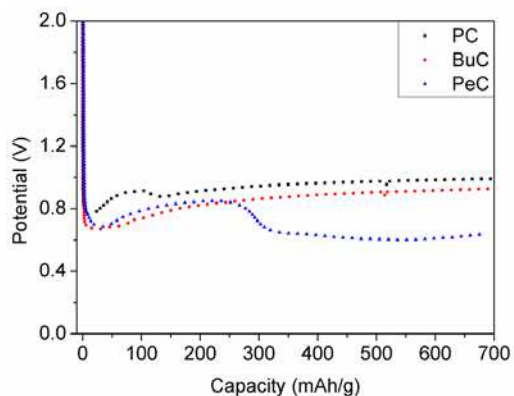
### Results and Discussion

Based on a literature procedure, cyclic carbonate derivatives are synthesized from epoxide and carbon dioxide catalyzed by chromium (III) salen catalyst. Product is purified via vacuum distillation, and stir over molecular sieves for 24 hours. Four different cyclic carbonate derivatives are synthesized and studied in this research (Scheme 1). Graphite electrode based half cells are tested using this series of derivatives as solvents or co-solvents with PC.



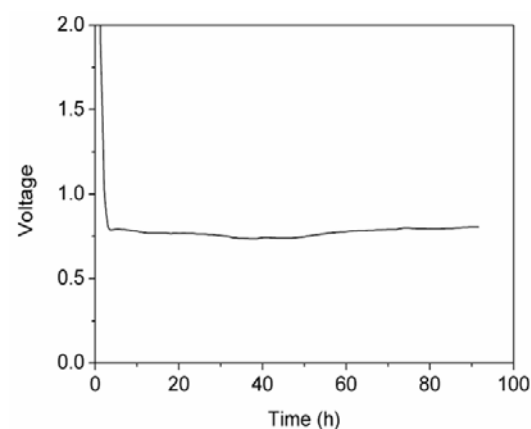
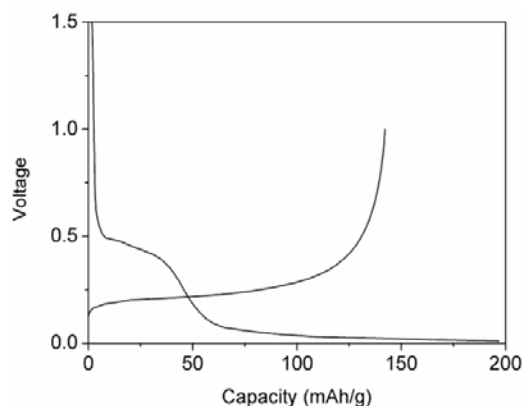
**Scheme 1.** Synthesis of substituted PC solvents.

As shown in Figure 1, PeC has the lowest potential (0.6 V) at the decomposition plateau, compared to BuC (1.0 V) and PC (1.1 V) in this study. PeC has the biggest steric hindrance of the three solvents, which needs a larger overpotential for co-intercalation.



**Figure 1.** The initial voltage profiles of PC and BuC and PeC with 1 M LiPF<sub>6</sub> at C/10 rate.

When the alkyl substituent is longer, such as in HeC and OcC, graphite exfoliation is prevented. We cycled cells in mixture of these solvents with PC at different ratios, it shows that HeC could prevent graphite exfoliation with a PC content as high as 25% (volume), higher PC ratio will cause exfoliation. OcC, with a longer alkyl substituents, could tolerate a PC content as high as 50% (volume).



**Figure 2.** (Top) 1st cycle voltage curve at C/10 and (bottom) voltage profile at C/100 in HeC/PC=4 in graphite based half cell with 1 M LiPF<sub>6</sub>.

Figure 2 shows cycling performance of graphite based half cell using the same solvent (HeC/PC=4) at different rates. At a relatively fast cycling rate (0.1 C, top figure), the solvated lithium ion could still be reversibly removed from graphite interlayer sites before PC decomposition, thus graphite exfoliation is avoided at a cycling rate of 0.1 C. However, when the cycling rate is slow (0.01 C, bottom figure), co-intercalated PC has enough time to obtain the electron and decompose, the decomposition product causes graphite exfoliation. The conductivity is comparable to single ion conductors described in the literature

### Conclusions

Similar to propylene carbonate, butylene carbonate and pentylene carbonate cause graphite exfoliation in the half cell. Cyclic carbonate derivatives with longer chain length, such as hexylene carbonate and octylene carbonate prevent graphite exfoliation. Cycling rate influence is preliminarily studied for HeC/PC co-solvent.

### Acknowledgement

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