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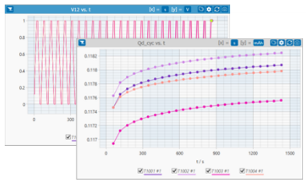

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Communication — The Impact of Co-solvent Selection for Dimethyl-2,5-dioxahexane carboxylate in Sodium Ion Batteries

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Traditional linear carbonates including dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) were investigated as co-solvents for the dimethyl-2,5-dioxahexane carboxylate (DMOHC)-based electrolyte in $Na_{0.97}Ca_{0.03}[Mn_{0.39}Fe_{0.31}Ni_{0.22}Zn_{0.08}]O_2$ (NCMFNZO)/hard carbon (HC) pouch cells. The EMC-containing cell displays excellent electrochemical performance, exhibiting only a 1.6 mAh irreversible capacity loss during 500 h of storage at 4 V and 40 °C, and maintaining over 80% capacity retention after 200 cycles up to 4 V at 40 °C. Severe gas evolution and Na plating issues are present in all the tested systems.

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The lifetime of sodium ion batteries (SIBs) still cannot meet the application requirements in grid energy storage systems, preventing them from serving as a viable alternative to lithium-ion batteries (LIBs).[1,2] Tuning the electrolyte components is considered as an effective way to promote the interphasial chemistries and properties which can mitigate side reactions between electrodes and electrolytes and extend cell lifetime.[3,4] Significant recent attention has been dedicated to electrolyte engineering in SIBs with the goal of extending cell lifespan.[5–8] Being different from the reported solvent chemistries, recent studies by Taskovic et al.[9,10] have demonstrated that the use of dimethyl-2,5-dioxahexane carboxylate (DMOHC, Fig. 1) as the solvent can dramatically improve the lifetime of $LiFePO_4$/graphite (LFP) and $Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_2$/graphite cells. However, DMOHC's functionality is constrained to high temperatures (>70 °C) due to its high viscosity (i.e. 6.93 cP at 25 °C).[9] It's important to note that not every battery necessitates operation in such a high temperature environment. The incorporation of co-solvents into DMOHC becomes essential to reduce viscosity, enabling functionality without the need for extreme temperatures. Traditional linear carbonates (Fig. 1), such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC), are commonly employed as co-solvents with low viscosity (i.e. DMC: 0.59 cP at 20 °C, EMC: 0.65 cP at 25 °C, DEC: 0.75 cP at 25 °C) to modulate electrolyte bulk properties.[9,11,12] Komaba et al.[13] studied the influence of these co-solvents on the electrochemical performance of a hard carbon (HC) anode when combined with ethylene carbonate (EC). However, limited studies exist on the impact of DMOHC on cell electrochemical performance when mixed with various co-solvents in SIBs.

By utilizing $Na_{0.97}Ca_{0.03}[Mn_{0.39}Fe_{0.31}Ni_{0.22}Zn_{0.08}]O_2$ (NCMFNZO)/HC pouch cells, we studied the cell electrochemical performance with different DMOHC-based electrolytes when DMC, DEC, and EMC served as co-solvents. Our results suggest increased sodium inventory loss during long-term cycling when DMC was employed as a co-solvent.

Experimental

Factory-manufactured 210 mAh NCMFNZO/HC pouch cells, without electrolyte, were obtained from Lifun Technology (Zhuzhou, Hunan, China). Detailed cell information can be referred to the previous reports.[14,15] According to 1:1 volume ratio, DMOHC (>98%, H_2O < 20 ppm, TCI) was mixed with selected co-solvents (>99.5%, H_2O < 20 ppm, CapChem) including EMC, DEC and DEC to form 1 m $NaPF_6$ (> 98.0%, H_2O < 20 ppm, TCI) electrolytes. 2% fluoroethylene carbonate ((FEC), >99.5%, H_2O < 20 ppm, Gotion) was used as an electrolyte additive in all the electrolytes. The procedure of pouch cell formation and scanning electron microscopy (SEM) testing are consistent with previous work.[15] After the formation, the cells were discharged to 1.5 V and charged to 4.0 V twice using C/20 at 40 °C before the 500 h storage at open circuit voltage. Cells were cycled after storage according to the previous procedure at 40 °C.[15] The amount of gas generated in the cells during formation, storage and cycling was determined through the application of Archimedes' principle, as detailed in the work by Aiken et al.[16] The electrochemical impedance spectroscopy (EIS) data, collected using a Biologic VMP3, involved ten data points per decade within the frequency range of 100 kHz to 100 mHz. The signal amplitude was set at 10 mV, and the measurements were conducted at 25 °C.

Results and Discussion

The effect of different linear carbonate co-solvents on the cell formation was quantified by gas volume evolution (Fig. 2A) and charge transfer resistance (R_{ct}, Fig. 2B). All the EIS spectra were measured at 3.1 V and room temperature. 2% FEC was added as a film-forming electrolyte additive in each cell. During cell formation at 40 °C with an upper cut-off voltage of 4 V, DMC generates more gas than DEC and EMC. According to the Nyquist plot with equivalent circuit fitting (Fig. 2B), the R_{ct} of DMC containing cell is much smaller compared to that of DEC and EMC after formation.

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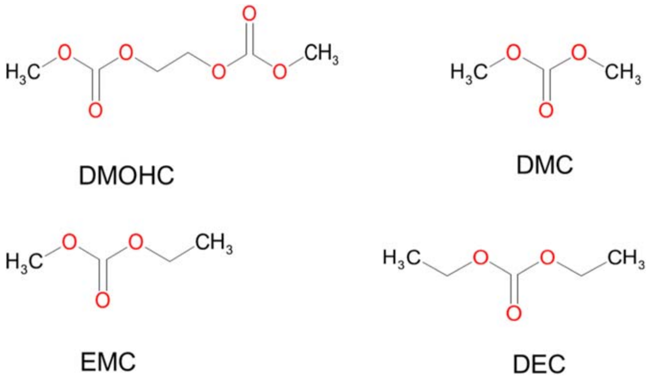

Figure 1. Chemical structures of selected solvents.

After formation, the cells were cycled twice at C/20 before storing under open circuit conditions for the next 500 h at 4.0 V and 40 °C. After 500 h of storage, the storage cells underwent two additional cycles with a current applied at C/20 to evaluate the extent of capacity loss experienced during the storage period. The critical parameters outlined by Sinha et al.[17] for a storage test include the discharge capacity before storage (D_0), the discharge capacity immediately after storage (D_1), the discharge capacity of a fully charged cell after storage (D_2), and the voltage drop (V_{drop}) during storage, as illustrated in Fig. 2C. According to Sinha et al.,[17] D_1 starts with the smallest capacity and at the lowest potential, attributable to the storage interval. D_2, featuring a larger capacity than D_1, suggests the recovery of some reversible capacity loss during storage. However, D_2 displays a smaller capacity than D_0, indicating irreversible capacity loss. In Table I, the EMC containing cell shows the smallest irreversible capacity (D_0-D_2) compared to that of DEC and DMC. Figure 2D shows that the EMC containing cell has the least potential variations during the open circuit 500 h storage at 40 °C. Per the Li inventory model by Sinha et al.,[17] this suggests that the inclusion of EMC may suppress electrolyte oxidation and potential shuttles, potentially facilitating the formation of a stable cathode electrolyte interphase (CEI).

The volume of gas evolution was recorded after 500 h storage at 40 °C as shown in Fig. 2E. Regardless of the chosen co-solvents, significant gas production was observed in all cells. Figure 2F shows the post-storage Nyquist plot of the cells in Fig. 2B. R_{ct} of EMC containing cells only increased by 43.68 $\Omega \cdot cm^2$ after storage, a smaller change compared to DMC (57.46 $\Omega \cdot cm^2$) and DEC (71.93 $\Omega \cdot cm^2$) containing cells.

In order to test the effect of selected co-solvents on the cycling lifetime of these SIBs, the pouch cells after storage were tested between 1.5 and 4.0 V at 40 °C and C/3 with C/20 check-up cycles every 50 cycles. Figure 3 shows the discharge capacity (A), and voltage polarization (B) as a function of cycle number for various co-solvent-containing cells. The capacity retention ranking is EMC>DEC>DMC (Fig. 3A), which is consistent with previous storage testing (Fig. 2D). All the cells tested here show a capacity retention >80% after 200 cycles (Fig. 3A). Surprisingly, the DMC containing cell shows slower polarization growth compared to DEC and EMC containing cells during cycling (Fig. 3B). Figure 3C shows the post-cycling Nyquist plot of the cells in Figs. 3A–3B. R_{ct} of DMC containing cell (222 $\Omega \cdot cm^2$) is smaller compared to EMC (274.5 $\Omega \cdot cm^2$) and DEC (302.5 $\Omega \cdot cm^2$) containing cells, aligning with the results in Fig. 3B. To identify the reason for the lower

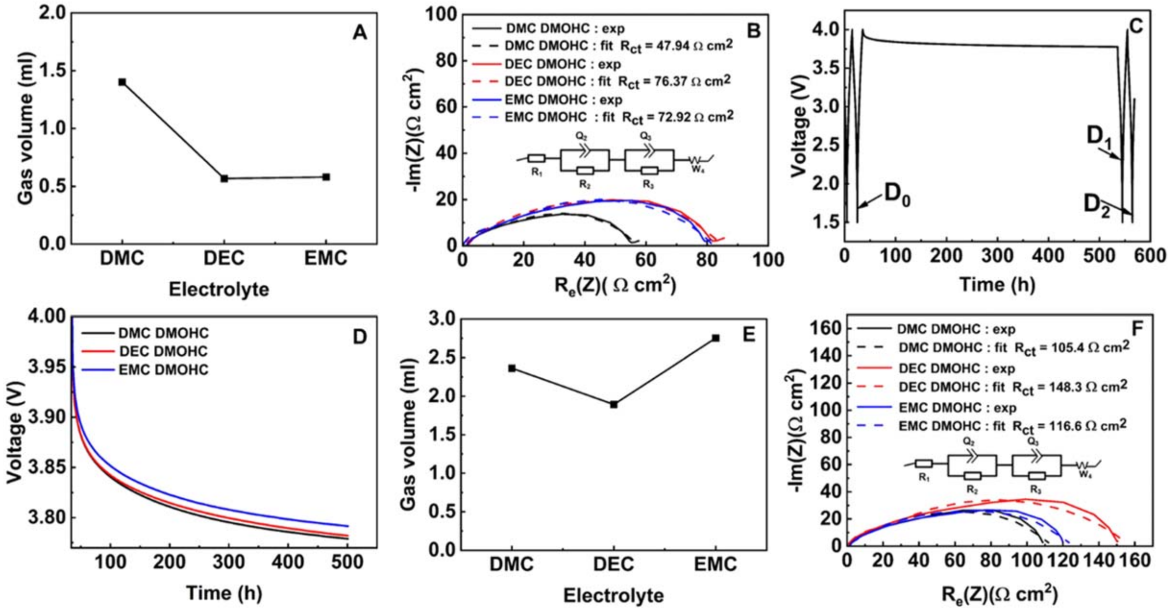

Figure 2. Evaluation of the effects of co-solvents during formation and storage. (A) Gas evolution during cell formation; (B) the Nyquist plot after cell formation measured at 3.1 V and room temperature; (C) a schematic of storage testing voltage vs. time profile; (D) voltage vs. time during 500 h storage testing at 40 °C and 4 V; (E) gas evolution during 500 h storage testing; (F) the Nyquist plot after cell 500 h storage testing measured at 3.1 V and room temperature. In the equivalent circuit model, Q is constant phase element, W is Warburg diffusion element, R_1 is solution resistance, R_2 is charge transfer resistance, R_3 is contact resistance.

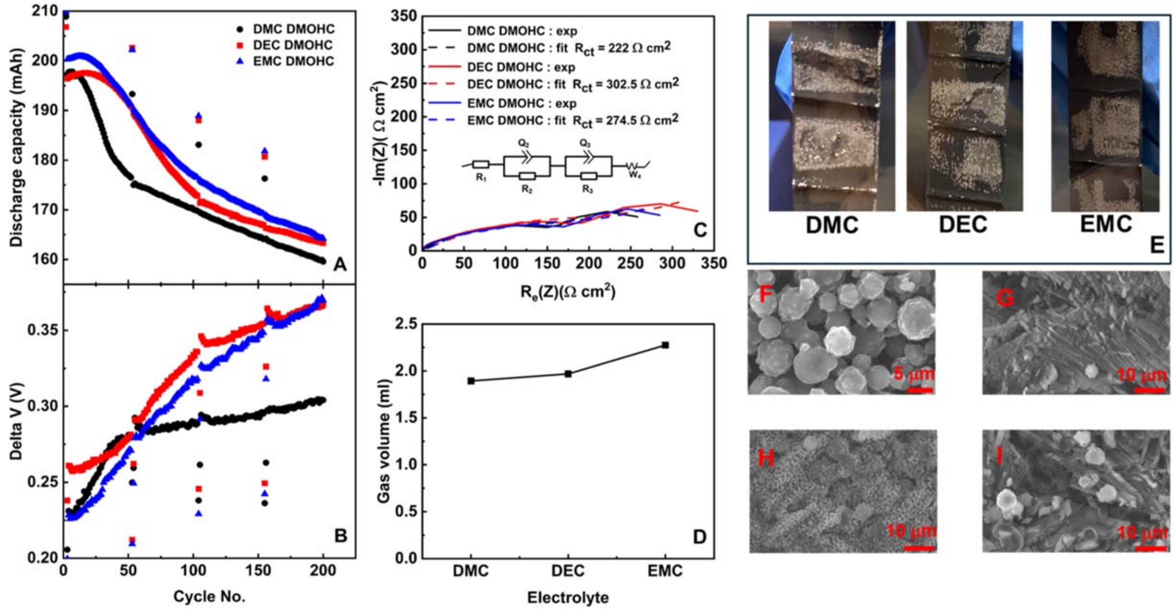

Figure 3. Evaluation of the effects of co-solvents during long-term cycling testing. (A) Discharge capacity, and (B) delta V vs cycling No. during long-term cycling between 1.5 and 4 V at 40 °C and C/3. C/20 was performed every 50 cycles. (C) The Nyquist plot after long-term cycling measured at 3.1 V and room temperature. (D) Gas evolution during long-term cycling. (E) HC anode picture with Na plating after long-term cycling. (F-I) SEM images of (F) fresh HC anode and Na plating part on the HC anodes after cycling with different co-solvents including (G) DMC, (H) DEC, and (I) EMC.

Table I. A summary of D_0, D_1, D_2 during 500 h storage testing.

Electrolyte	D_0 (mAh)	D_1 (mAh)	D_2 (mAh)
DMC	201	188.4	194.1
DEC	198.1	186.7	190.2
EMC	201.5	191.6	199.9

capacity retention in the DMC-containing cell, a careful examination was performed on the check-up cycling results at C/20 (Fig. 3A). A notable capacity drop, possibly due to Na inventory loss, is evident in the DMC-containing cell compared to EMC and DEC-containing cells at the C/20 cycling rate (Fig. 3A), mitigating polarization disturbances. This suggests an inferior interphase formation when DMC is used as a co-solvent, leading to increased side reactions between electrodes and electrolytes, resulting in Na inventory loss. As a common degradation product of electrolytes,[9,18] DMOHC is unlikely to undergo decomposition and contribute to the formation of SEI and CEI. The cross reactions and carbonate transesterification between linear carbonate (e.g. DMC, DEC, EMC) and cyclic carbonate (e.g. FEC)[19,20] are encouraged to study to understand the detailed SEI/CEI formation mechanism here. Figure 3D shows the continuous generation of a substantial amount of gas in all cells during long-term cycling.

The cycled pouch cells were then disassembled and the HC anodes were exposed to Ar in the glovebox to visually check for Na plating. Figure 3E shows photographs of the HC anodes from the pouch cells cycled with DMC, DEC, and EMC as co-solvents. Noticeably, a significant amount of Na plating is observed, potentially contributing to cell failure in this study. Ball-shaped HC particles (Fig. 3F) were observed to be embedded within plated sodium, as evidenced by thorough SEM analysis (Figs. 3G–3I).

Conclusions

In this work, we compared the effect of DMC, DEC and EMC as co-solvent with DMOHC in NCMFNZO/HC pouch cells using EIS, storage and long-term cycling testing. The electrode/electrolyte interphase formed with DMC is inferior, leading to increased side reactions and Na inventory loss. Although EMC demonstrates improved calendar and cycling lifetime performance with some impedance control, challenges related to gas evolution and Na plating still require attention for further improvements of lifespan in SIBs.

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