A morphological study of SEI film on graphite electrodes

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Abstract

Morphological features of the protective layer on the graphitic electrodes, formed by reduction of electrolytic solution components during the first cycle, are investigated by SEM and common electrochemical techniques. As expected, the interaction between electrode and solution is very important, leading to quite different results for different solutions. Here, results for solution of various solvents ratio are reported. It appears that the performances of the electrodes are strongly dependent on their surface chemistry in solutions. We can conclude that the nature of the surface film plays a key role for the electrode stability or to capacity decrease always related to an increase of the electrode itself impedance. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In lithium-ion batteries graphitic and carbon anodes are regarded as a valid choice to lithium in the field of energy storage and conversion devices. In particular, for graphites is well known that lithium-ions are reversibly intercalated into graphenes planes according to a series of well-defined stages till the complete lithiation at LiC_6 [1,2]. So that, to make this process reversible and with a good capacity for an high number of cycles, it is necessary to avoid the exfoliation phenomenon [3,4] arising from cointercalation, between graphitic layers, of solvent molecules. This is possible by the formation on the electrode surface of a thin protective film which allows only ion migration, leaving out the solution species [5,6].

In fact, it is known that on the surfaces of these electrodes, during the first cycle before the lithium insertion, the electrolytic solution reduction brings about the deposition of a solid electrolyte interface (SEI) film, that plays a fundamental role in assuring electrodic good life and long cyclability. This process is accompanied by an irreversible capacity loss and the reversible capacity stabilises typically after the first few cycles. Formation conditions, e.g. the working temperature of SEI influence the different performances of the same material. For many devices, the operating temperature can reach even 55°C and this may critically influence the choice of the solution. Many authors have studied by several techniques (FTIR [7], XPS [8], AFM [9,10]), the chemical composition of the passivating film, which appears to be basically formed of insoluble lithium salts (as $LiCO_3$ and $(CH_2OCO_2Li)_2$) [5,11], enable to prevent the solvent cointercalation. According to the results, the major role is played by ethylene carbonate (EC), whose presence assures the rapid film formation and then prevents other undesirable side reactions [12]. In this work a series of SEM pictures are presented, which show the superficial changes on the electrodes under several conditions of SEI growth and electrochemical treatment. The $LiPF_6$ EC/DMC or EC/DEC mixtures, which are the electrolytes most widely employed in commercial lithium-ion batteries, induce some difficulties upon long cyclation at high temperature, because of the evaporation of DMC or DEC and to probable corrosive effects caused by the presence of HF, deriving from salt decomposition.

The aim of this work is to find the best solution for high temperature operation, by determining the minimum EC/propylene carbonate (PC) ratio to avoid graphite exfoliation. Results for cell assembled with $LiClO_4$ EC/PC 2/1 and $LiBF_4$ EC/PC 3/1, respectively, are reported compared with those obtained with the $LiPF_6$ EC/DMC 1/1 reference solution.

2. Experimental

Natural graphite NG-7 (Kansai Coke and Chemicals Co. Ltd.) was used as host material. Composite electrodes were

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prepared by mixing graphite and teflon aqueous emulsion (PTFE) in 97.5:2.5 wt.% ratio and then dried under vacuum overnight. The slurry obtained by mixing with ethyl alcohol was spread on a copper foil current collector. Coated electrodes were left to settle at about 80°C and then dried under vacuum at 120°C for approximately 60 min. The electrodes were not compressed prior to use for not modify the surface morphology.

Pure lithium metal foil was used as both the reference and counter electrodes. The electrolytic solutions were: (a) 1 M $LiClO_4$ (Aldrich) dissolved in a 2/1 (by volume) mixture of freshly distilled EC and PC (Fluka); (b) 1 M $LiBF_4$ (Tomiyama) dissolved in a 3/1 mixture of EC and PC; (c) 1 M $LiPF_6$ dissolved in EC/DMC 1/1 (Merck battery grade solution).

Galvanostatic cycles were carried out in the 1.2–0.05 V potential range at several rates by means of a MacPile system (Biologic). A conventional three electrode cell was used to run ac impedance measurements. Spectra were obtained by a Solartron 1255 frequency response analyser (FRA), coupled to a 1286 Solartron electrochemical interface, in the frequency range 1×10^5–1×10^{-1} Hz with an oscillating signal of 10 mV peak-to-peak on the equilibrium potential.

3. Results and discussion

Fig. 1, which shows first discharge (Li-intercalation) curves for different solutions, demonstrates the entity of the solvent decomposition reaction on the graphitic electrodes. The curve obtained with the $LiBF_4$ EC/PC 1/1 solution is also reported, from which the very enhanced decomposition reaction at 0.8 V with a 50% loss of reversible capacity is clearly seen. The same cell failed after few cycles. We had to lower the ratio EC/PC to 3/1 with $LiBF_4$ and 2/1 with $LiClO_4$ to achieve good results, i.e. only 20% of irreversible capacity. This value is very close to that obtained in $LiPF_6$
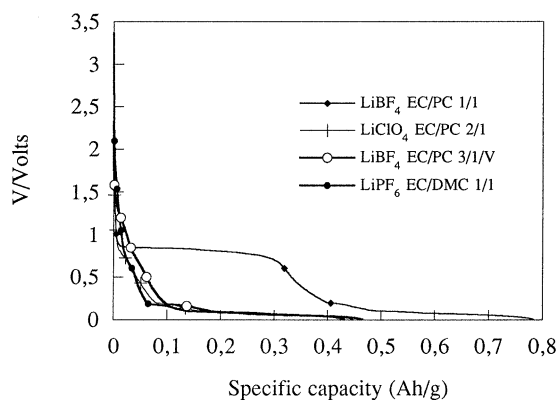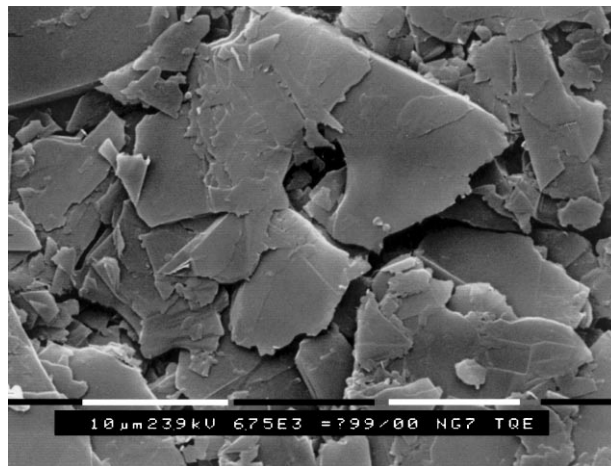

Fig. 2. SEM micrograph of a composite graphite electrode surface prior to any electrochemical treatment.

EC/DMC. The results for the different solutions will be discussed separately.

Fig. 2 shows the SEM picture of a composite electrode before any electrochemical treatment to better appreciate the surface modification after cycling in the $LiBF_4$ EC/PC 3/1 solution. Fig. 3 shows the SEM micrograph of the same electrode after the first anodic charge ($i = 0.25$ mA/cm²) at 25°C. The formation of the SEI film is clearly shown. In fact, comparing with Fig. 2, the surface is covered of a thick layer of film which loses its uniformity after cell failure (Fig. 3b). Fig. 3c is reported the surface of the electrode after cyclation at 55°C. The dramatical effect of temperature on the surface is revealed by the fact that the SEI film is completely destroyed. On the other hand, Fig. 4 which shows cycles performed at 25 and 55°C (0.25 mA/cm²), demonstrates that the trends were not too dissimilar in both cases, also if the film was damaged by above mentioned temperature effect. To verify the quality and stability of different types of SEI, we have stored cells under OCV conditions at room temperature, in the charged state (electrode completely intercalated). Fig. 5 summarises results for all the solutions used in this study. We can observe as low autodischarge in $LiBF_4$ EC/PC 3/1, revealed by the fact that the electrode works about 2 months to reach 0.2 V value at which is impossible to recover any charge.

Fig. 6 shows the electrode surface film freshly formed in the $LiClO_4$ EC/PC 2/1 solution at 25°C (Fig. 6a), its modifications after cycling (Fig. 6b) and after a storage period of 80 days at room temperature (Fig. 6c). The newly formed film has a morphology similar to that in the previous solution, but the electrodic electrochemical performances are better in term of cycle number. This is shown in Fig. 7, where, because of the high conductivity of this solution, the specific capacity increases as temperature increases. In addition, this solution provides long storage times before self discharge occurs (see Fig. 5). Impedance spectra, recorded during increasing storage time, are shown in
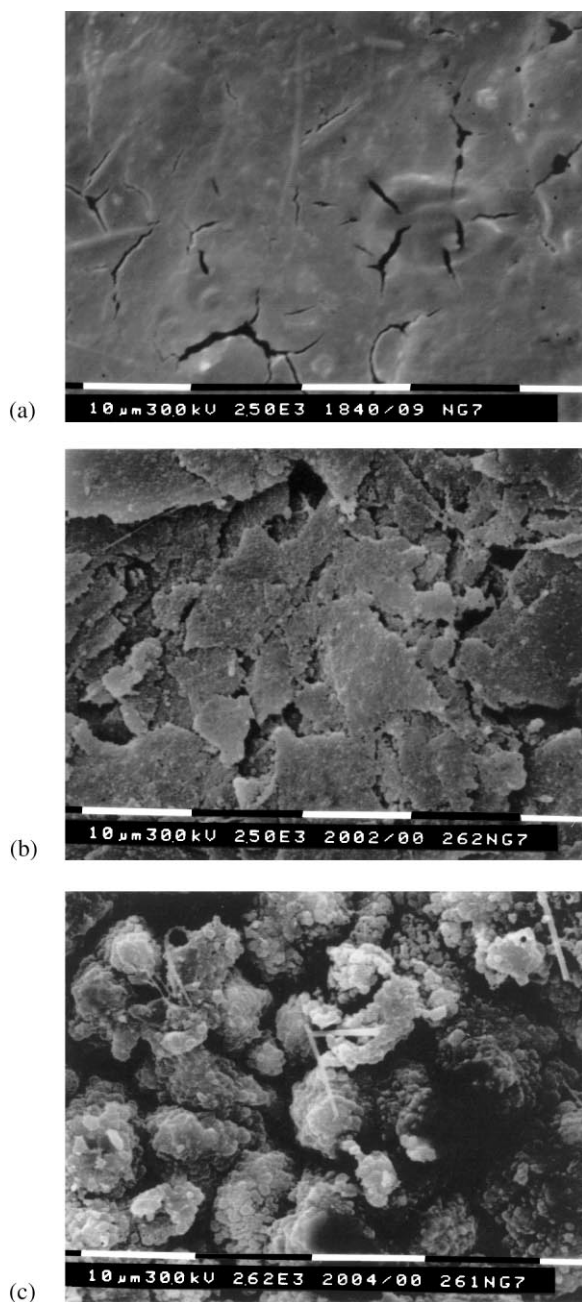

Fig. 1. Surface film formation on a composite graphite electrode in contact with different electrolytic solutions ($i = 0.25$ mA/cm²).

(a)

(b)

(c)

Fig. 3. SEM micrograph of a surface SEI film on a graphite electrode in LiBF$_4$ EC/PC 3/1 solution: (a) after the first discharge; (b) after prolonged cycling; (c) after cycling at $T = 55°C$.

Fig. 4. Cycling behaviour of a graphite electrode at 25 and 55°C in a LiBF$_4$ EC/PC 3/1 solution ($i = 0.25$ mA/cm^2).

Fig. 5. Open circuit voltage profile of electrodes stored in the charged state (fully intercalated) in different electrolytic solutions.

Accordingly, the high frequency semicircle observed in Fig. 8 may be attributed to the migration across the surface film and it is characterised by very low capacities, i.e. in the order of few μF. In Fig. 8, the total impedance slightly increases with days, reasonably because of film ageing. This fact seems to be confirmed by the variation of the depression angle, whose value is related to the roughness (porosity) of the surface. This conclusion is supported by Fig. 6c, which clearly shows the appearance of neoformations on the surface, whose morphology remain unchanged with time.

Fig. 8. Only one semi-circle is clearly detectable and then related. Values of depression angle, resistance and capacity are reported in Table 1 as determined on the basis of one *R–C* circuit at high frequencies.

According to Aurbach [5], one has to regard lithium intercalation as a multi-step process which involves: (1) migration of the lithium-ions across the film on the surface electrode; (2) their insertion in the carbonaceous material accompanied by the charge transfer at the interface carbon-film; (3) solid state diffusion into the bulk of the electrode.
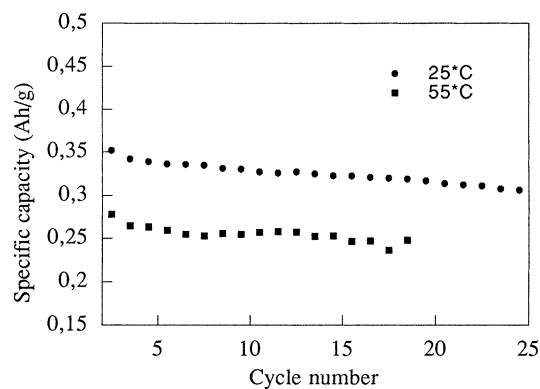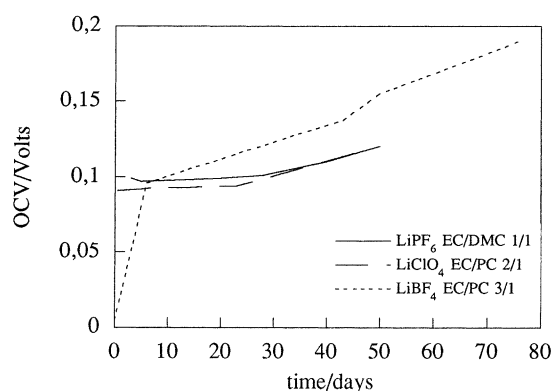
Table 1
High frequency impedance data for a graphite electrode sample kept in OCV conditions after the first discharge in the LiClO$_4$ EC/PC 2/1 electrolyte

OCV (V)	Depression angle	R (Ω)	C (F)
0.05	11.9	39.41	6.3×10^{-6}
0.096	18.7	45.1	6.2×10^{-6}
0.137	21.88	70.3	4.2×10^{-6}
0.155	26.22	80.9	3.8×10^{-6}

(a)

(b)

(c)
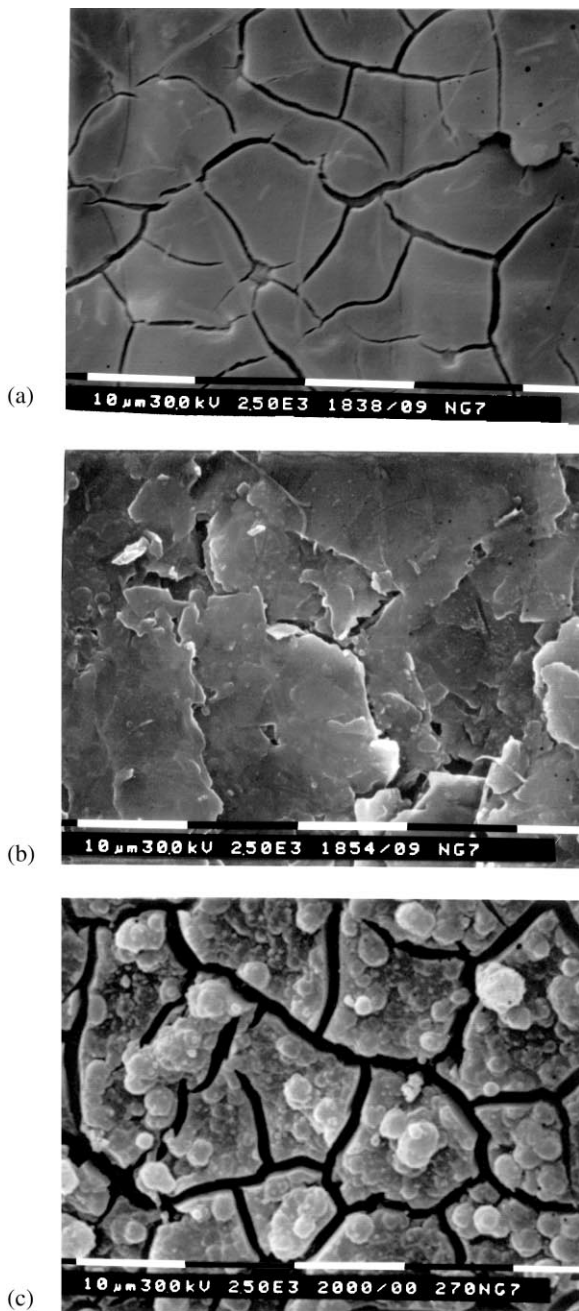
Fig. 6. SEM micrograph of surface SEI film on a graphite electrode formed in the LiClO$_4$ EC/PC 2/1 solution: (a) after first discharge; (b) after prolonged cycling; (c) after 50 days of storage at the charged state in OCV conditions.

Finally, Fig. 9 reports SEM micrograph of the film grown in a battery grade commercial solution of LiPF$_6$ EC/DMC. Fig. 9a shows that, different from the other samples, before cycling or storage tests, the film has not discontinuities probably because of the absence of PC in the testing solution. After electrochemical treatment (Fig. 9b and c), the film assumes the morphology observed in the previously analysed surfaces. In particular, Fig. 9c, which reports the appearance of the electrode surface after a long storage time
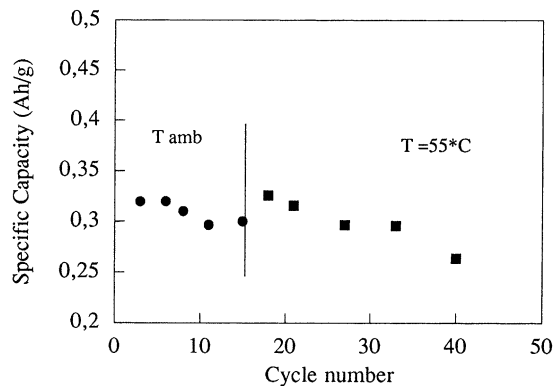

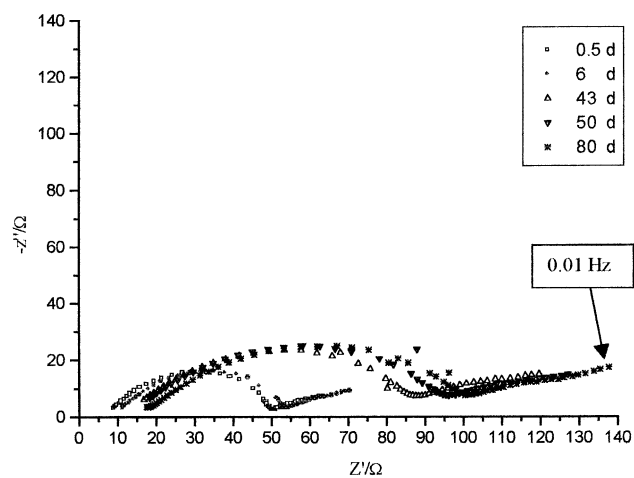Fig. 7. Cycling of a graphite electrode in LiClO$_4$ EC/PC 2/1 electrolyte ($i = 0.25$ mA/cm^2).

Fig. 8. Impedance spectra at increasing times of storage of a graphite electrode kept in the charged state under open circuit voltage conditions in the charged state.

(about 1 month), demonstrates that the globular structures are present in a large amount. A deeper analysis of such a morphology is in progress in our laboratory.

Fig. 10 which reports galvanostatic cycles in the LiPF$_6$ EC/DMC electrolyte, demonstrates that at 25°C the graphite electrodes stabilise to constant capacity values, while at 50°C, the capacity decreases rapidly below 0.2 Ah/g. A similar effect was found for manganese spinel electrodes when cycled at 50°C in the same electrolyte [13]. In this case, the rapid failure of this cathodes was attributed to the corrosive effect of HF, present as LiPF$_6$ decomposition product especially at temperatures above ambient. A similar cause may be also inferred for the case of the graphite electrode. All this considered, one can conclude that these electrodes are stable in the LiPF$_6$ EC/DMC electrolyte only at room temperature and that this stability is associated with the morphological features of the SEI film.
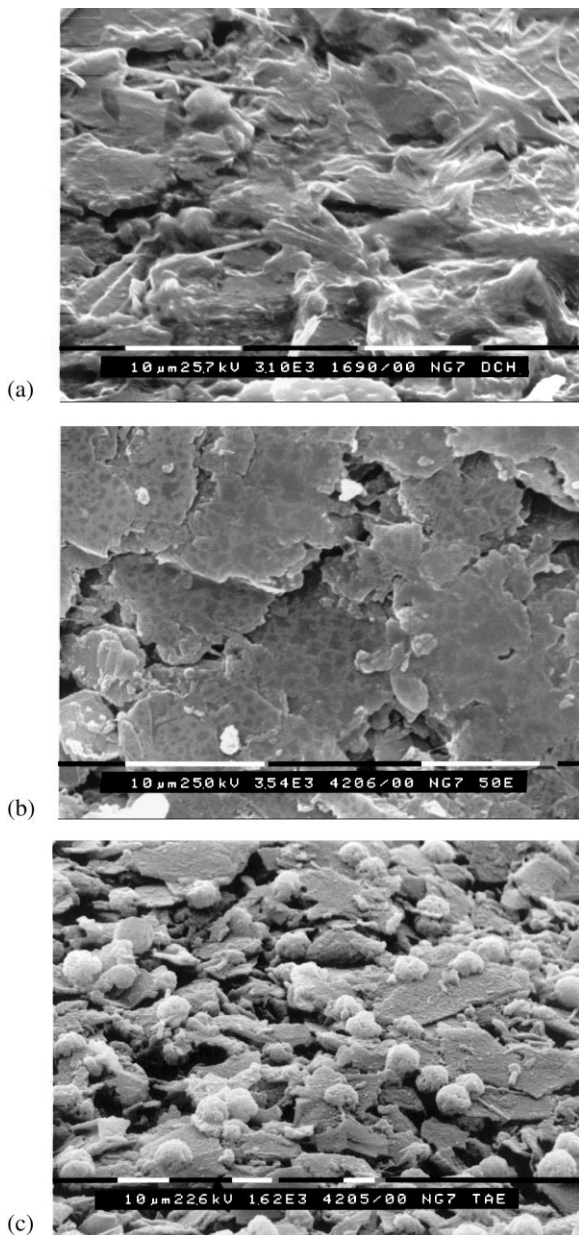
(a)

(b)

(c)

Fig. 9. SEM micrograph of surface SEI film on a graphite electrode in a LiPF$_6$ EC/DMC 1/1 solution: (a) after the first discharge; (b) after prolonged cycling; (c) after 50 days of storage in the charged state under OCV conditions.

4. Conclusions

Natural NG 7 graphite electrodes have been tested in three different solutions to investigate their ability of inducing protective and stable SEI film, also in high temperature working conditions. The film morphology was found to be very similar in the case of LiBF$_4$ EC/PC 3/1 and LiClO$_4$ EC/PC 2/1, clearly for the presence of PC in both cases. The film morphology after electrode failure appears substantially similar for both solutions. It seems evident that the film break-down is responsible for the electrodes failure, allowing the percolation of solution inside the graphite bulk.
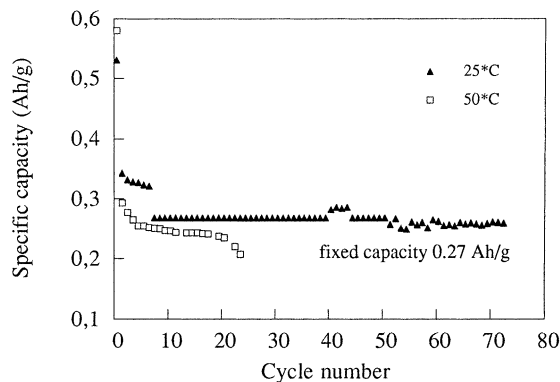

Fig. 10. Cycling behaviour of a graphite electrode at 25 and 55°C in LiPF$_6$ EC/DMC 1/1 ($i = 0.25$ mA/cm^2).

Impedance spectra have demonstrated that, with storage time, the diffusion of lithium-ion through the SEI becomes increasingly more difficult and then that the total impedance increases. Accordingly, we can outline the two undesirable consequences of the presence of PC in the electrolyte solution: (1) not homogeneous passivation of the electrode surface layer; (2) the electrode destroying action due to solvent cointercalation. However, the LiClO$_4$ EC/PC solution seems to allow reasonable cycling response at high temperature, while in the LiPF$_6$ EC/DMC solution the cycling performance decays quite rapidly.

Acknowledgements

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