Reversible sodium metal plating/stripping in a fluorine-free electrolyte

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Alkaline metals are gathering much attention as a high-capacity negative electrode for high-energy-density rechargeable batteries. However, their poor reversibility and dendritic growth have long been a barrier to practical application. Generally, an electrolyte solution is an important factor that dominates the reversibility of alkaline metal electrodes; in particular, fluorine is considered to be one of the essential elements to form a fluorine-containing protective layer that stabilizes the electrode/electrolyte interphase[1,2]. Fluorinated salts/solvents, however, are not suitable from the view point of green chemistry. Hence, a new class of fluorine-free electrolyte for alkaline metals is needed.

Herein, we report a fluorine-free electrolyte using sodium tetraphenylborate ($NaBPh_4$) and 1,2-dimethoxyethane (DME). The BPh_4 anion is supposed to be stable, because the active boron atom is surrounded by four stable phenyl groups. Figure 1 shows the coulombic efficiencies of sodium metal plating/stripping in 0.1 M $NaBPh_4$ / DME or 1.0 M $NaPF_6$ / EC/DEC electrolyte. In the $NaBPh_4$ electrolyte, the coulombic efficiency rapidly reached 99.9 %, which was significantly higher than in the $NaPF_6$ / EC/DEC electrolyte. The excellent reversibility was kept over 300 cycles. The SEM image (the inset in Fig. 1) shows that the sodium metal plated in the $NaBPh_4$ electrolyte was non-dendritic, round shape. These results indicate better compatibility of this electrolyte with a sodium metal negative electrode. This work suggests that fluorine is not an element of definite necessity to stabilize alkaline metal negative electrodes, and promotes the research and development of safe and environmentally-benign fluorine-free electrolytes.

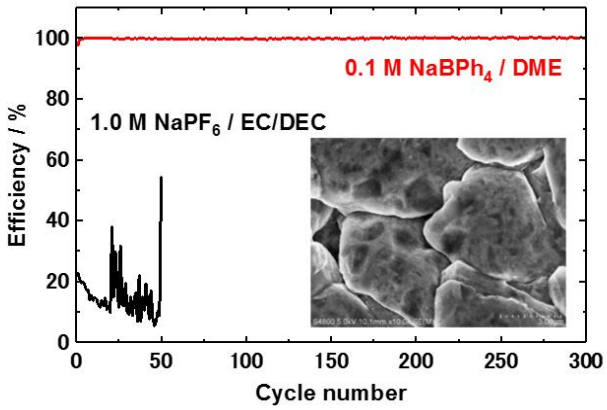

Figure 1. Coulombic Efficiencies of sodium metal plating/stripping on Cu foil in $NaBPh_4$/DME and conventional electrolyte obataiend by the garvanostatic measurement of Cu/Na cells at 0.5 mA cm^{-2}. A certain amount of sodium metal corresponding to 0.5 mAh cm^{-2} was plated and then stripped to the cutoff voltage of 0.5 V. The inset shows the SEM image of sodium metal plated in the $NaBPh_4$ electrolyte.

References:

[1] K. Xu, Chem. Rev. 114 (2014) 11503–11618.
[2] Z.W. Seh, J. Sun, Y. Sun, Y. Cui, ACS Cent. Sci. 1 (2015) 449-455.