

Supporting Information for “Rechargeable Ca-ion Batteries: A New Energy Storage System”

By

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Scanning electron microscopy was taken to determine the particle morphology of the as prepared MFCN (Figure S1). The particles are on the order of $1\mu\text{m}$ with some larger particles present. They have a rectangular prismatic shape, which is consistent with strong faceting along the $\{100\}$ planes.

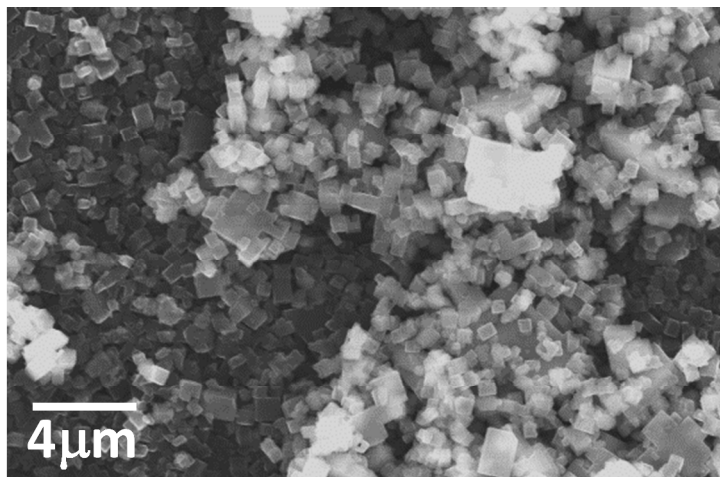


Figure S1. Scanning electron micrograph using 30 keV electrons of as prepared MFCN.

NMR spectra were recorded at ambient temperature for $\text{Ca}(\text{PF}_6)_2$ in 3:7 EC:PC electrolyte to determine the salt's purity. ^{19}F NMR shifts were referenced to $\text{BF}_3\text{-OEt}_2$ (-153 ppm) and ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4 (0 ppm). As shown in Figure S2 and S3, both the ^{19}F and ^{31}P NMR of $\text{Ca}(\text{PF}_6)_2$ in the EC/PC mixed solution suggest the purity of this salt in the electrolyte, including the detection of the doublet ^{19}F NMR signal at -73.1 ppm with the $^2J_{\text{P-F}} = 708.4$ Hz, and the observation of a set of septet signal for ^{31}P NMR at -144.5 ppm with the $^2J_{\text{P-F}} = 708.7$ Hz.

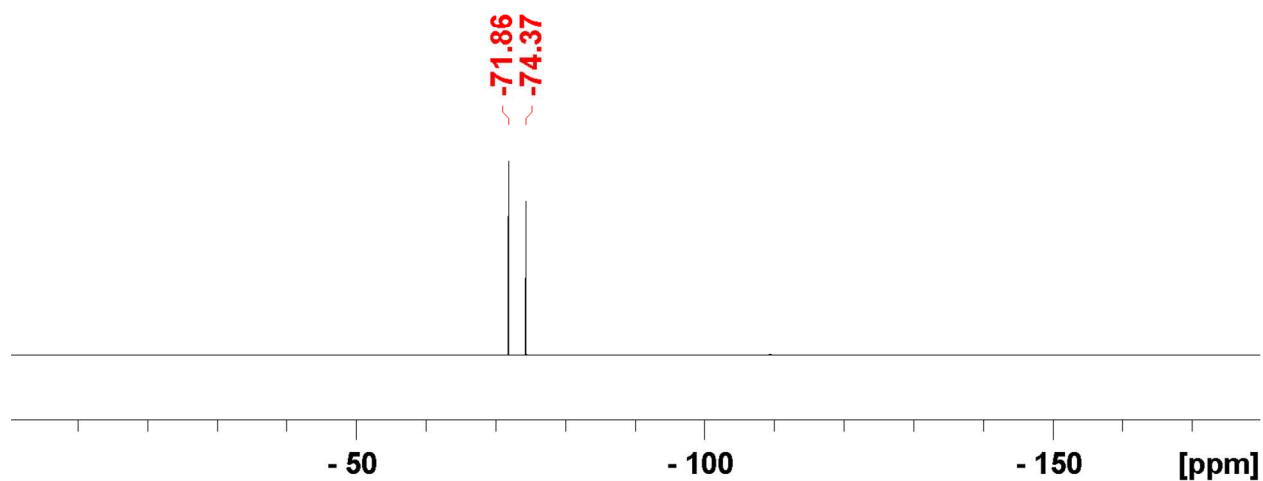


Figure S2. ^{19}F NMR of $\text{Ca}(\text{PF}_6)_2$ in EC/PC, $J_{\text{P-F}} = 708.4$ Hz

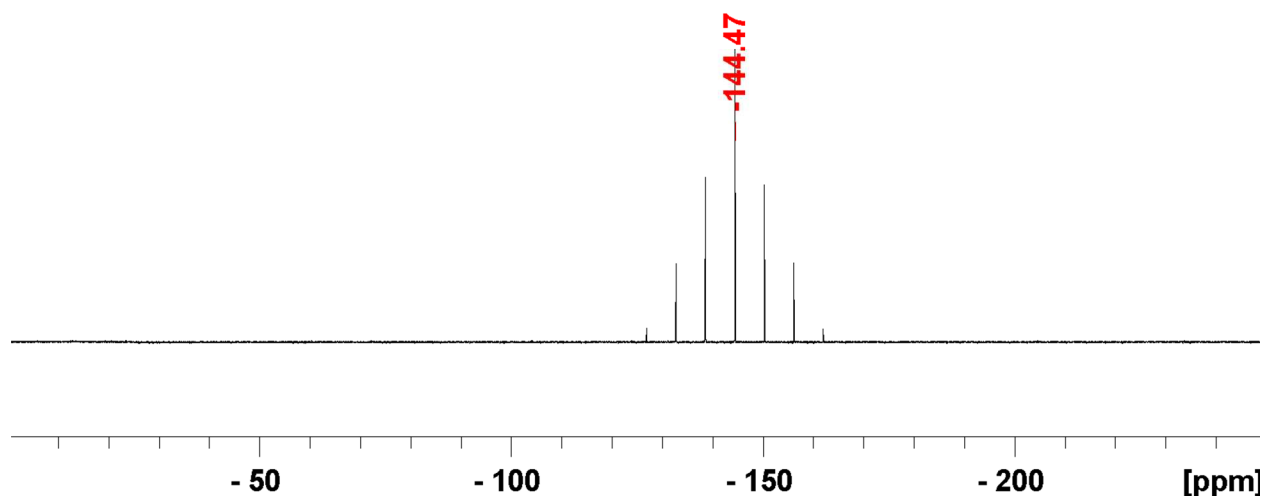


Figure S3. ^{31}P NMR of $\text{Ca}(\text{PF}_6)_2$ in EC/PC, $J_{\text{P-F}} = 708.7$ Hz.

Since the Ca metal pseudo-reference does not assume the standard potential of Ca/Ca^{2+} in the Ca electrolyte, ferrocene was added to the electrolyte to calibrate the potential. The resulting CV is shown in Figure S4. The ferrocene redox potential is at approximately 2.8V vs. Ca metal. However, ferrocene has a standard potential of 0.64V vs. standard hydrogen electrode or about 3.5V vs. Ca/Ca^{2+} . This indicates that adding 0.7V to the voltage vs. Ca metal will give the voltage vs. Ca/Ca^{2+} .

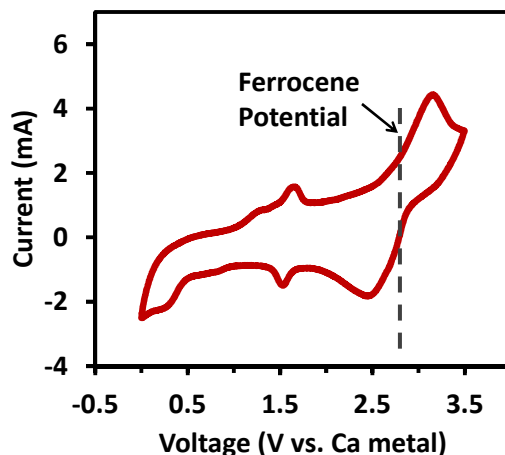


Figure S4. CV with a Ca metal pseudo-reference using 0.2M $\text{Ca}(\text{PF}_6)_2$ in 3:7 EC:PC electrolyte with ferrocene added, carbon black working electrode and a BP2000 carbon counter electrode.

A 3-electrode CV of tin is shown in Figure S5. Ca appears to be reacting with tin below about 2.4 V, but the highest current peak is at about 1 V vs. Ca/Ca^{2+} . There are oxidation peaks at approximately 2.5 V that likely correspond to the removal of Ca from the Sn, which is consistent with the main plateau for the discharge of MFCN vs. tin being at about 0.8 V. This CV is consistent with a surface film forming on the surface giving rise to an overpotential for removing Ca.

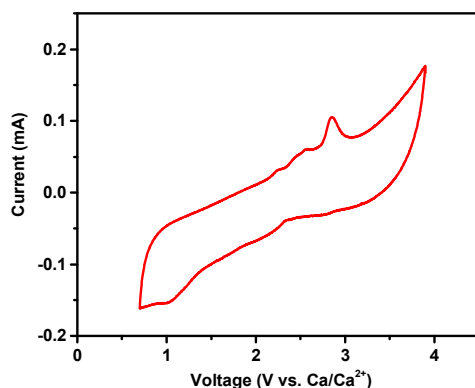


Figure S5. CV of tin using a Ca metal reference corrected using the ferrocene calibration. The electrolyte was 0.2M $\text{Ca}(\text{PF}_6)_2$ in 3:7 EC:PC and the counter electrode was BP2000 carbon.

Figure S6 shows the discharge curve of a Sn electrode using Ca metal as the anode. The capacity for the tin is about 40 mAh/g. There are clearly 2 voltage plateaus indicating that the Ca and Sn are forming at least 2 distinct local environments.

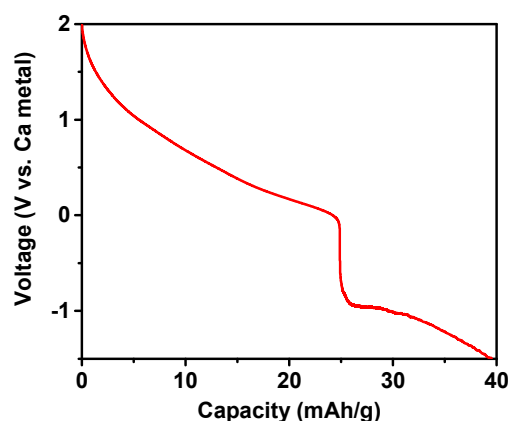


Figure S6. Discharge curve of a Sn electrode vs. Ca metal using 0.2M $\text{Ca}(\text{PF}_6)_2$ in 3:7 EC:PC electrolyte.

The first charge curve of the MFCN-Sn system is shown in Figure S7. This curve is mostly indicative of side reactions, which are likely the formation of passivation films on the electrode surfaces.

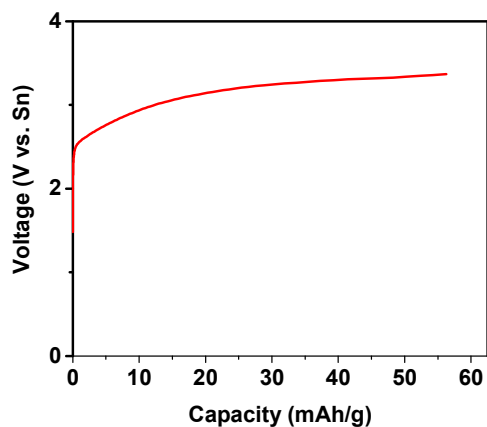


Figure S7. First cycle charging of the desodiated MFCN cathode with a Sn anode using 0.2M $\text{Ca}(\text{PF}_6)_2$ in 3:7 EC:PC.

EDX spectra of a discharged and charged MFCN cathode that has been cycled against a calciated tin anode is shown in Figure S7. The calcium content of the discharged sample is substantially higher than that of the charged sample indicating reversible insertion of Ca into the structure. There is also a small quantity of tin present on or in the cathode material, which points towards the corrosion of the tin anode during cycling.

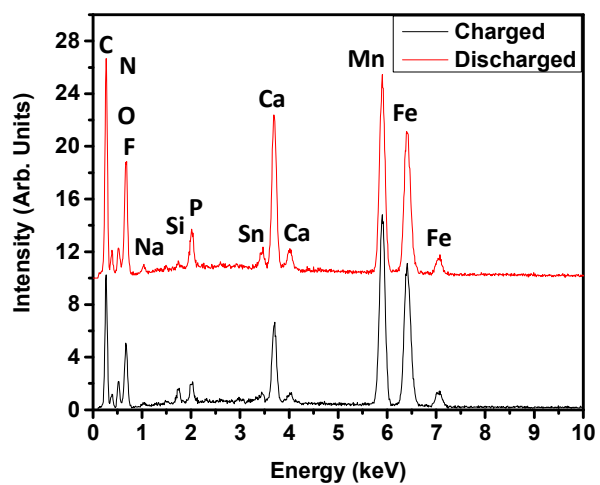


Figure S7. Ex situ EDX spectra of desodiated MFCN that has been charged then discharged against calciated tin (discharged) and another sample that was charged, discharged and then charged.