

Interactions of Silicon Nanoparticles with Carboxymethyl Cellulose and Carboxylic Acids in Negative Electrodes of Lithium-Ion Battery

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1. CMC-Na spectra

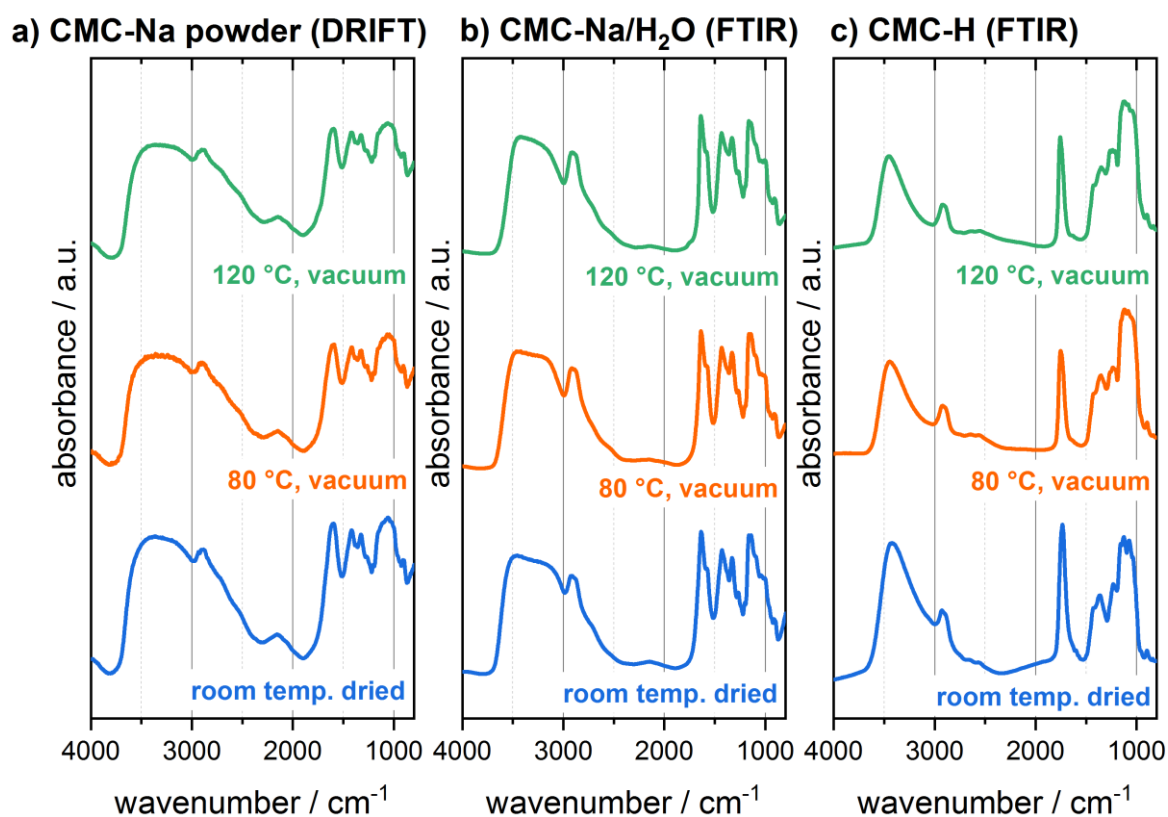


Figure S-1. IR spectra of CMC-Na powder measured by DRIFT and cast-film of CMC-Na measured by FTIR in the wavenumber range of 4000-800 cm⁻¹. Three different drying conditions were examined: room temperature dried/stored samples (bottom, blue), drying overnight under vacuum at 80 °C (middle, orange) and at 120 °C (top, green).

2. Tabulated values for characteristic IR shifts

Table S-1. Characteristic IR shifts in the region between 1400 – 1800 cm⁻¹ of the samples prepared and examined in this study.

sample	technique	Drying conditions	Absorption bands / cm ⁻¹			
			v _s COO ⁻	v _{as} COO ⁻	δH ₂ O	vC=O
CMC-Na powder	DRIFT	RT	1415	1595	- ^s	
		80 °C, vac	1415	1591	- ^s	
		120 °C, vac	1415	1591	- ^s	
CMC-Na/H ₂ O (cast film)	FTIR	RT	1431	1577	1637	
		80 °C, vac	1431	1577	1637	
		120 °C, vac	1431	1577	1637	
CMC-H (cast film)	FTIR	RT	1419			1730
		80 °C, vac	1419			1751
		120 °C, vac	1419			1757
Glycolic acid (GlyAc)	DRIFT	RT	1431			1757/1730
		80 °C, vac	1419			1768/1745
		120 °C, vac	1419			1768/1745
Malic acid (MalAc)	DRIFT	RT	1444/1409		- ^s	1737/1691
		80 °C, vac	1444/1409			1737/1691
		120 °C, vac	1417			1745
Citric acid (CitAc)	DRIFT	RT	1419			1755/1724/1693
		80 °C, vac	1427			1741/1706
		120 °C, vac	1427			1741/1703
CMC-Na/GlyAc	FTIR	120 °C, vac	1421	1610		1743
CMC-Na/Gly-buffer	FTIR	120 °C, vac	1456	1581	1635	1753
CMC-Na/MalAc	FTIR	120 °C, vac	1433	1600		1766/1704
CMC-Na/Mal-buffer	FTIR	120 °C, vac	1433	1600		1760/1704
CMC-Na/CitAc	FTIR	120 °C, vac	1438			1768/1704
CMC-Na/Cit-buffer	FTIR	120 °C, vac	1444	1591		1758/1681
Si + GlyAc	DRIFT	80 °C, vac	1411	1583	1647	>1700 ^s
		120 °C, vac	1411	1583	1639	>1700 ^s
Si + Gly-buffer	DRIFT	80 °C, vac	1415	1604		1716
		120 °C, vac	1417	1625		
Si + MalAc	DRIFT	80 °C, vac	1402	1604		1726
		120 °C, vac	1402	1604		1726
Si + Mal-buffer	DRIFT	80 °C, vac	1411/1398	1604		1732
		120 °C, vac	1413	1612		1728
Si + CitAc	DRIFT	80 °C, vac	1408	1608		1730
		120 °C, vac	1408	1608		1730
Si + Cit-buffer	DRIFT	80 °C, vac	1409	1598		1718
		120 °C, vac	1433/1406	1620/1585		1724
Si+CMC-Na (pH=7)	DRIFT	80 °C, vac	1417	1606		1708 ^s
		120 °C, vac	1419	1608		1731 ^p
Si+CMC-H (pH=2.5)	DRIFT	80 °C, vac	1419	1604	1639	1743
		120 °C, vac	1419	1608		1749
Si + Gly-buffer + CMC-Na	DRIFT	80 °C, vac	1415	1604		1730/1716
		120 °C, vac	1421	1614		1747

Si + Mal-buffer + CMC-Na	DRIFT	80 °C, vac	1415-1394	1604	
		120 °C, vac	1421	1608	1735
Si + Cit-buffer + CMC- Na	DRIFT	80 °C, vac	1409	1598	1732
		120 °C, vac	1407	1604	1726

^s shoulder in neighbouring peak

^b broad

^p plateau

3. Si reference spectra

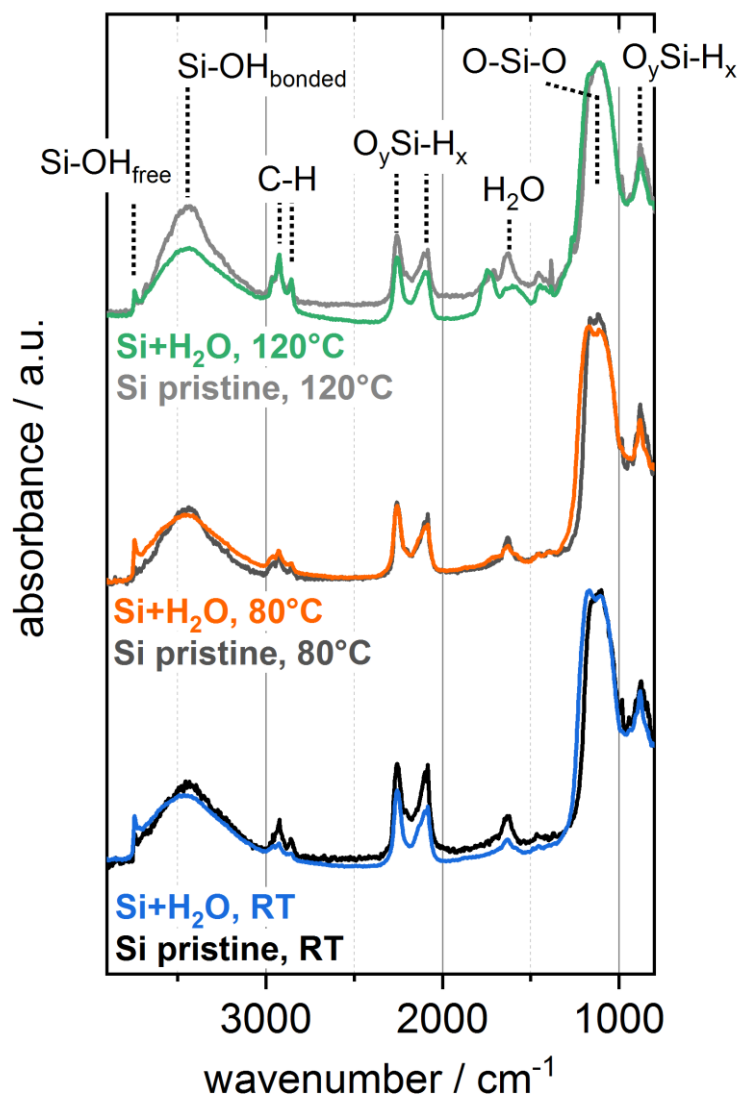


Figure S-2. DRIFT spectra of silicon nanoparticles dried at room temperature (black/blue), 80 °C + vacuum (darkgrey/orange) and 120 °C + vacuum (grey/green). The pristine samples were used as received and dried at the respective temperatures. For Si+H₂O samples the silicon nanoparticles were dispersed in water prior to drying.

4. DRIFT spectra of undried and dried carboxylic acid powders

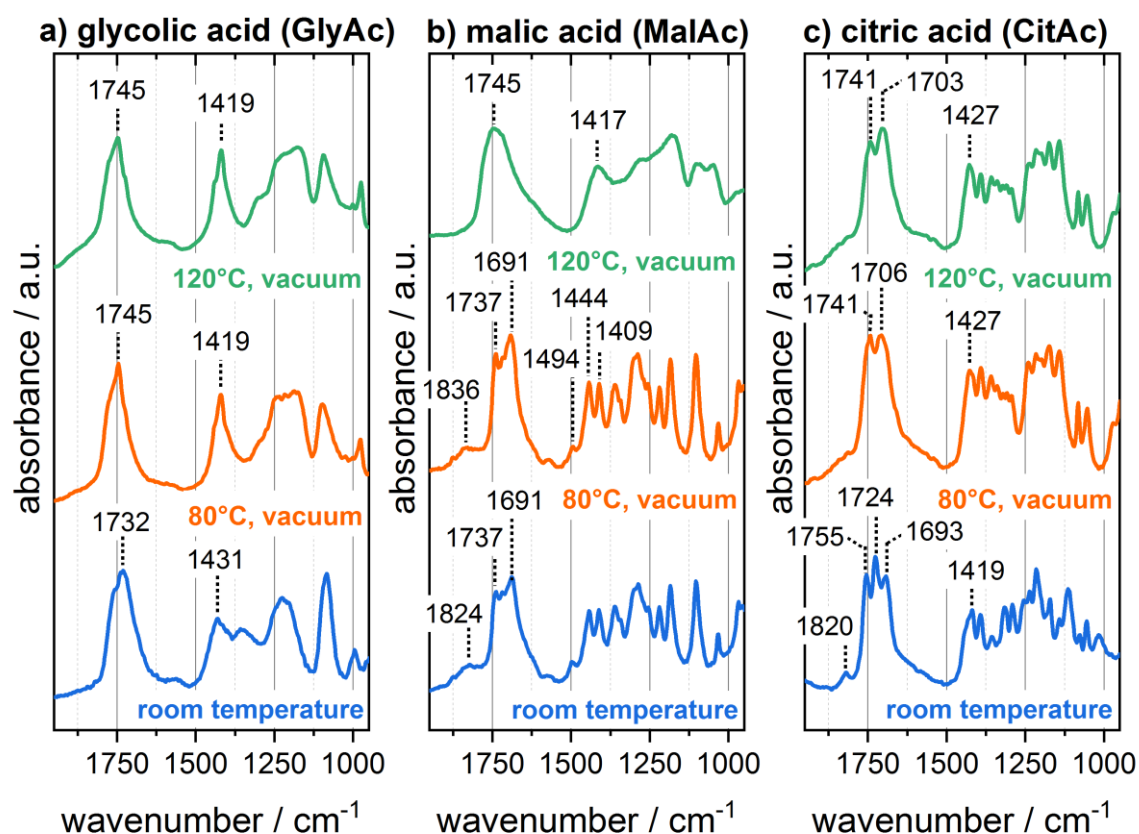


Figure S-3. DRIFT spectra of glycolic acid (a, GlyAc), malic acid (b, MalAc) and citric acid (c, CitAc) powders. The as received powders (blue) were dried at 80 °C + vacuum (orange) as well as 120 °C + vacuum (green).

5. DRIFT spectra of silicon samples treated with carboxylic acids and binder at 80 °C

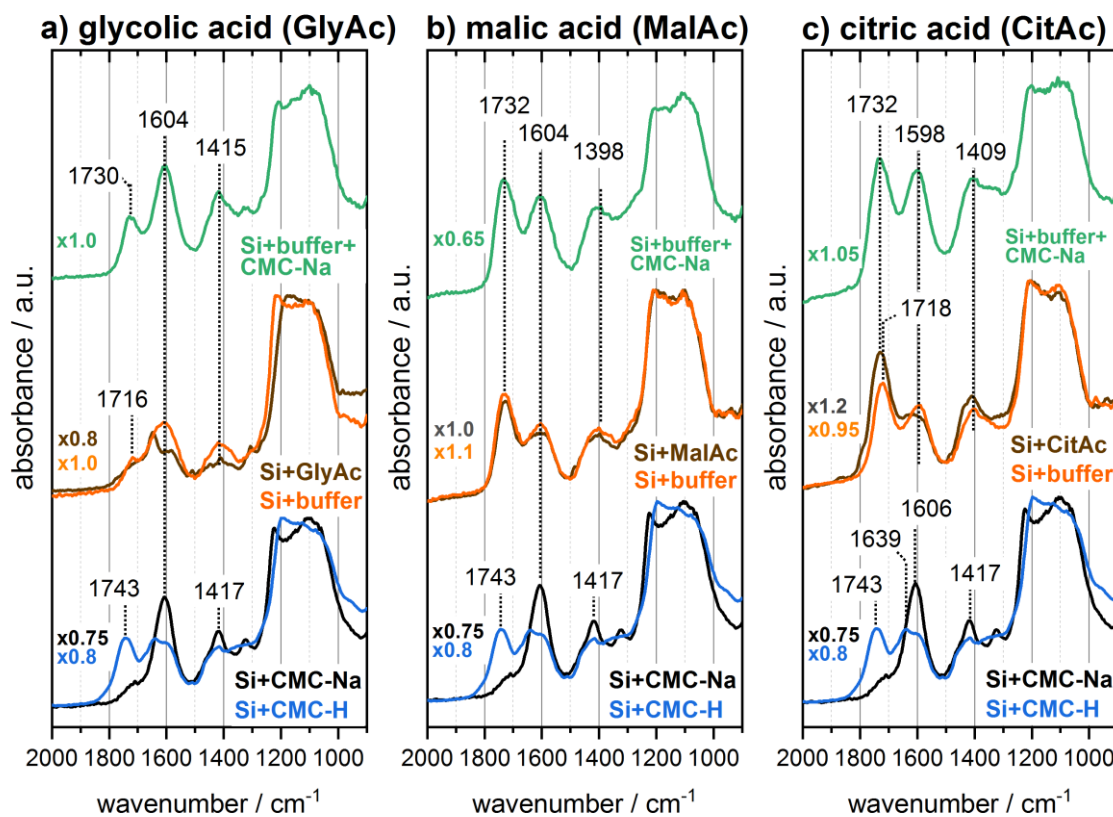


Figure S-4. DRIFT absorption spectra of silicon nanoparticles treated with a CMC-Na or a CMC-H solution (pH=7, black and blue), a solution of the respective carboxylic acid (pH<3, brown), a buffer solution (pH=3, orange) and a solution comprising buffer and CMC-Na (pH=3, green), respectively. Carboxylic acids: glycolic (a), malic (b) and citric (c). The samples were dried at 80 °C under vacuum prior to the measurement.

6. Expanded FTIR spectra of cast CMC-Na films

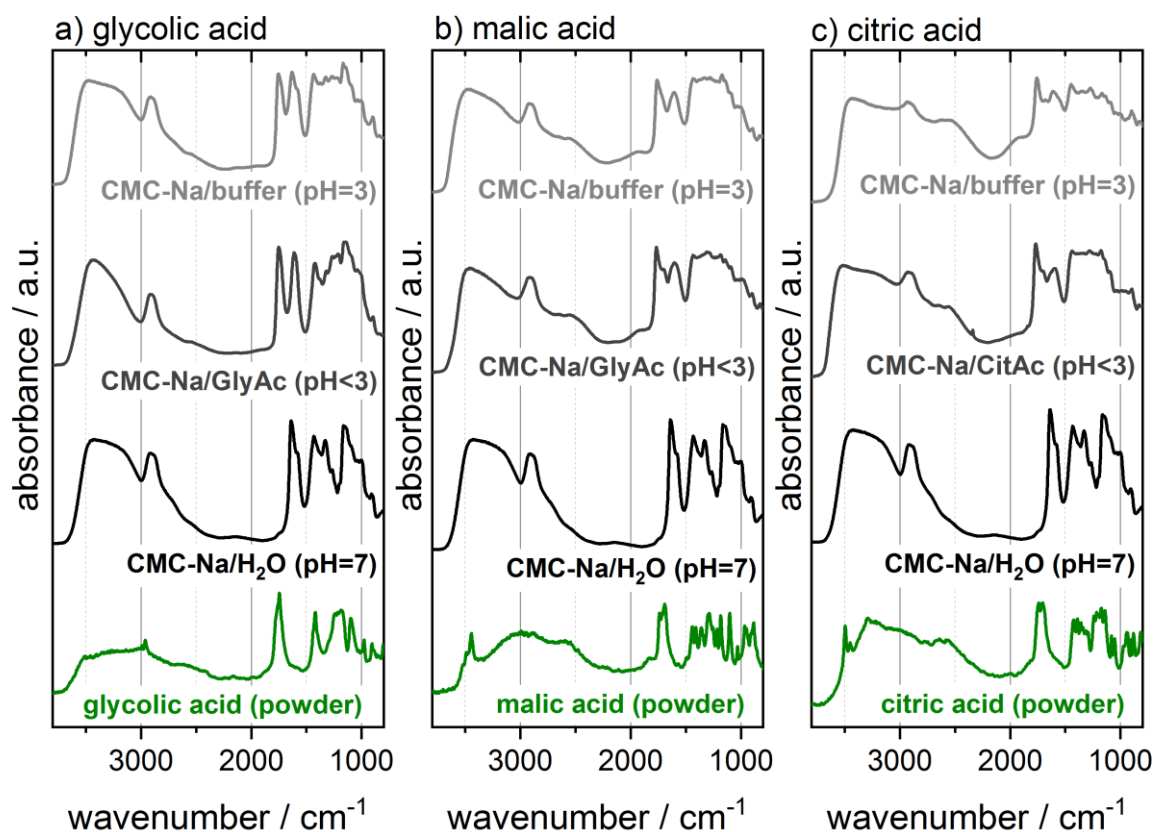


Figure S-5. FTIR spectra of cast CMC-Na films in the wavenumber region of 800–3800 cm^{-1} . CMC-Na solutions containing any of the carboxylic acids (dark grey line, 2nd from top) or the corresponding buffers (grey line, top) have been cast on a glass substrate and were dried first at room temperature and then overnight at 80 °C under reduced pressure. For better comparison a CMC-Na film cast from a solution of deionized water (pH = 7) has also been added in each panel (black line, 2nd from bottom). The reference spectrum of the corresponding carboxylic acid (green line, bottom) has been recorded with the pre-dried pristine powders using DRIFT.

7. Coulombic Efficiencies (Fig. 5)

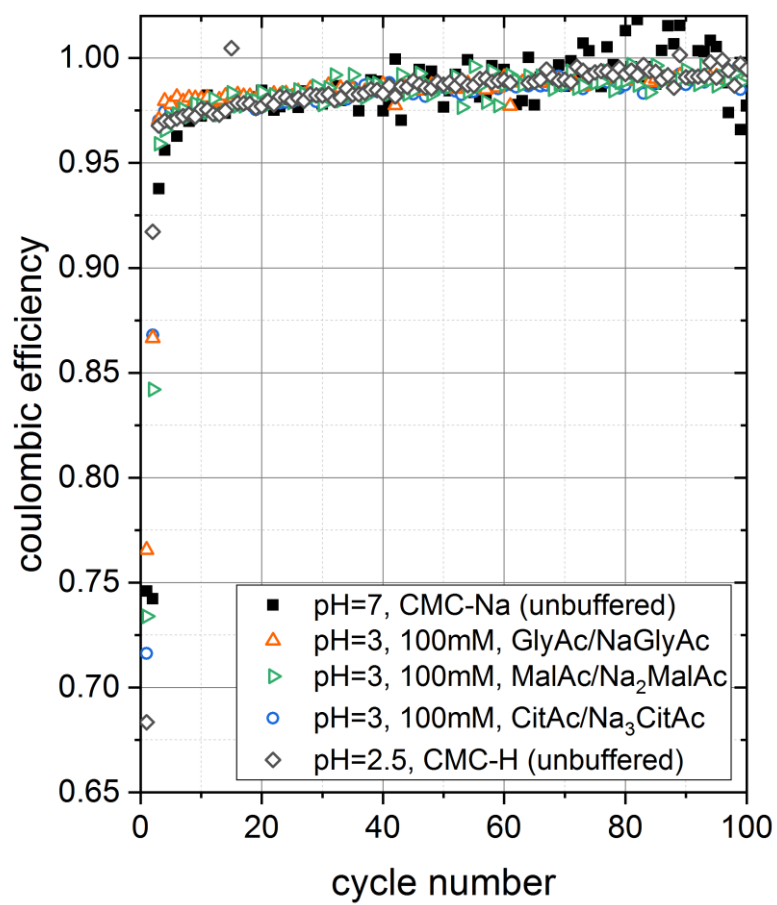


Figure S-6. Coulombic efficiency vs. cycle number (top) of the galvanostatic cycling data presented in Figure 5.

8. Electrochemical Data

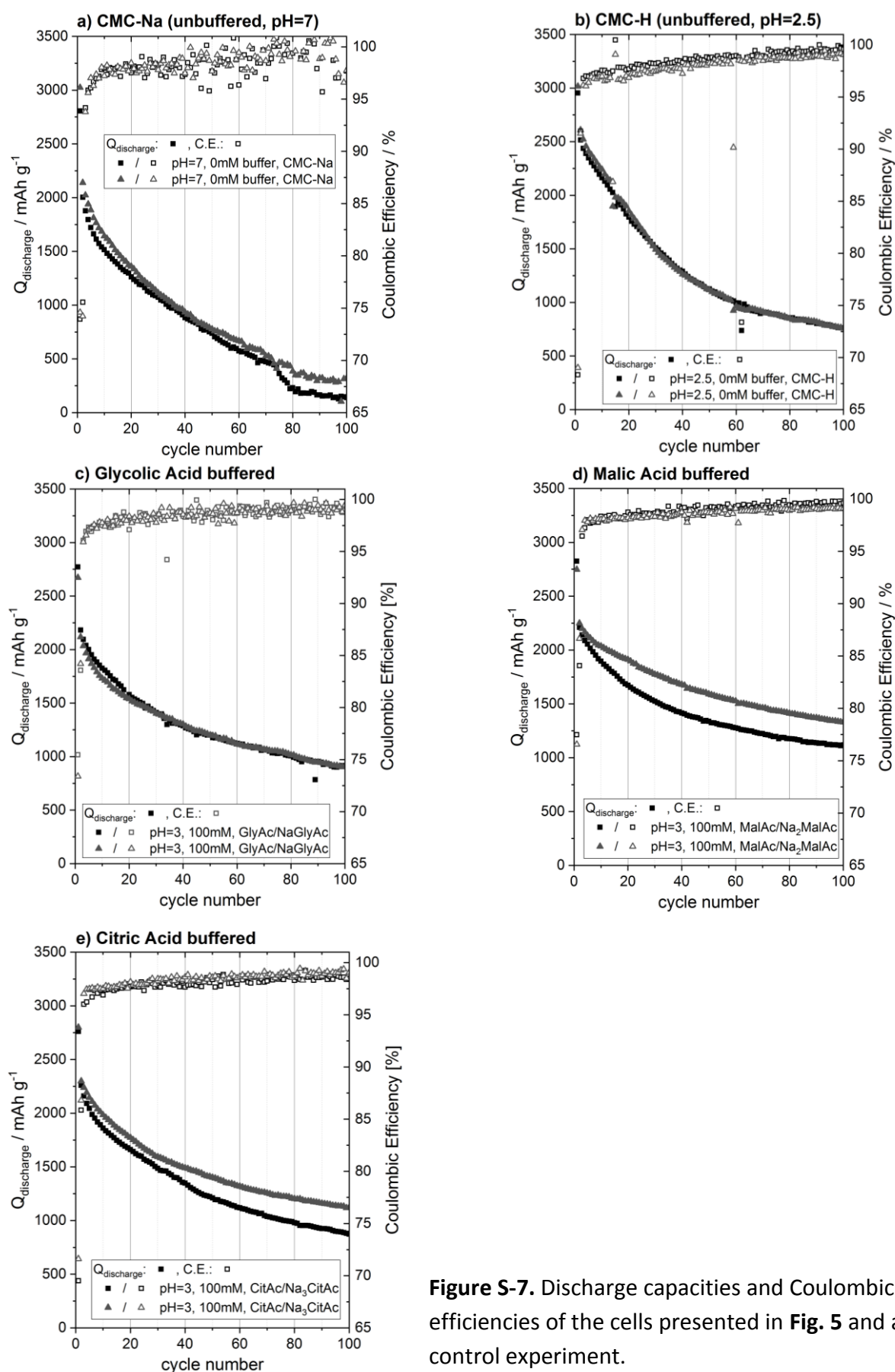


Figure S-7. Discharge capacities and Coulombic efficiencies of the cells presented in **Fig. 5** and a control experiment.

9. dQdE Analysis

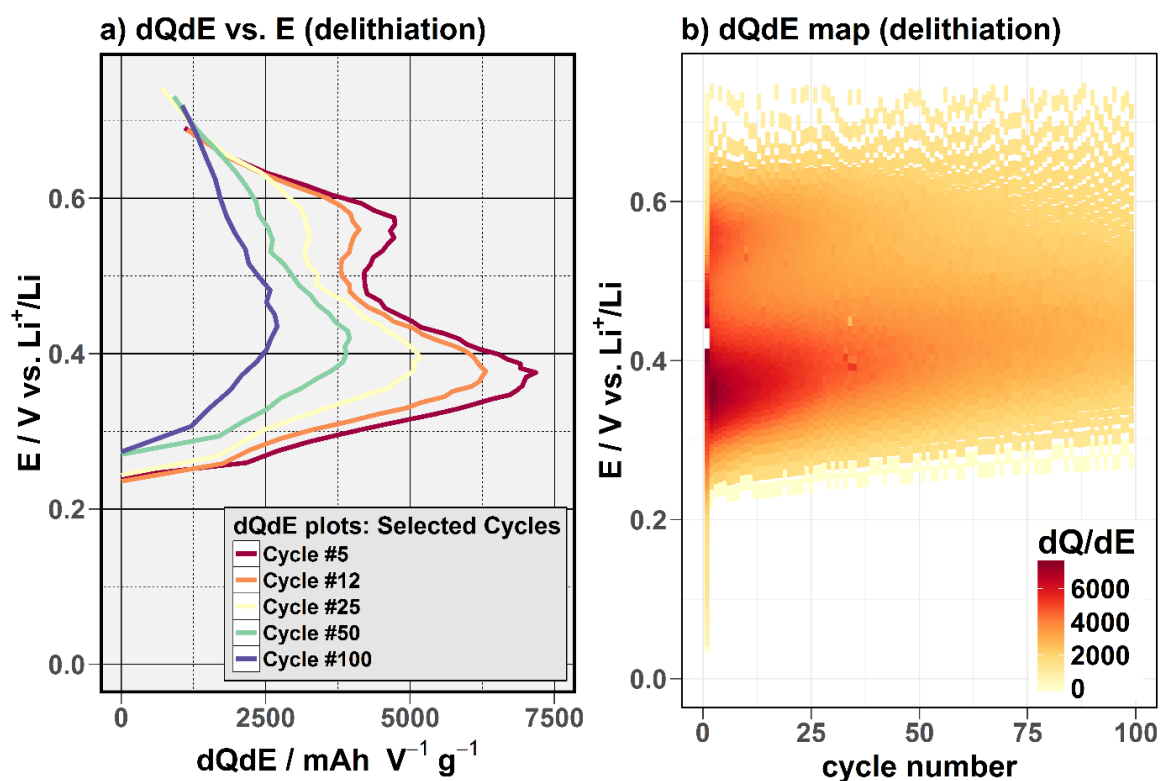


Figure S-8. Example: From dQdE plots of selected cycles to dQdE maps

dQdE maps: Lithiation

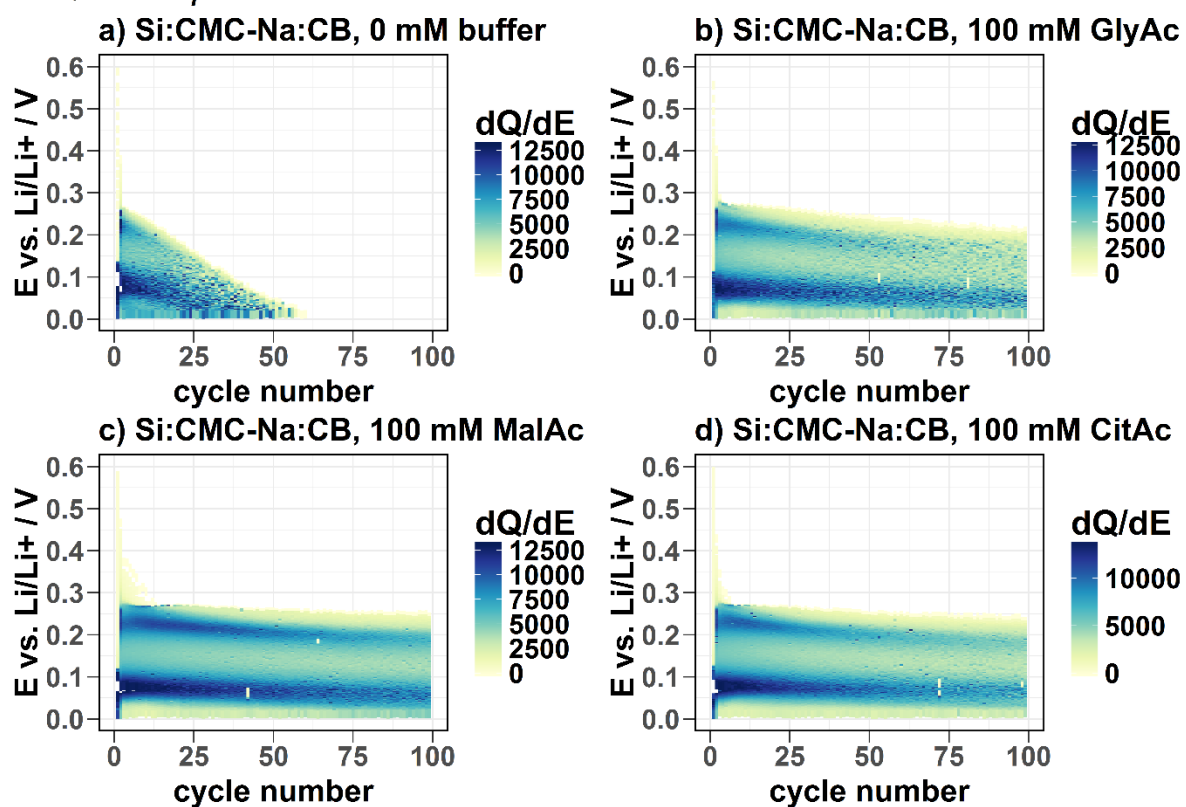


Figure S-9. dQdE maps of the lithiation process

10. Voltage Profiles

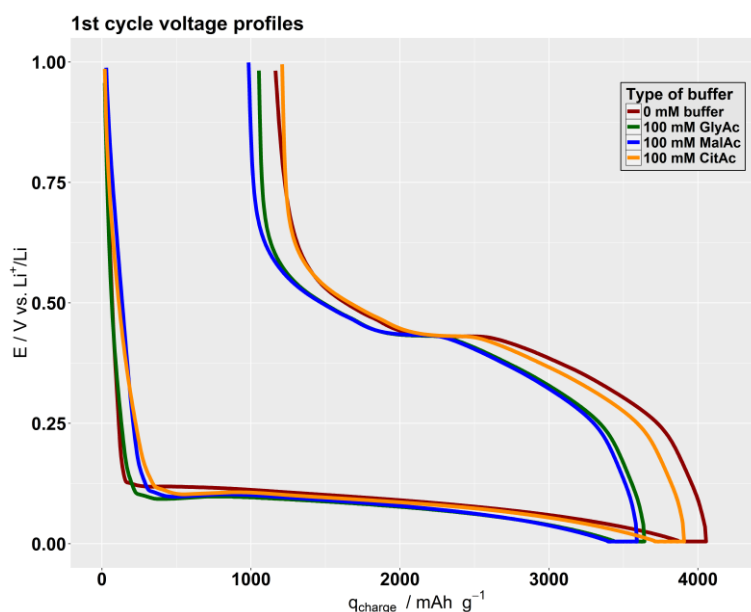


Figure S-11. First cycle voltage profiles

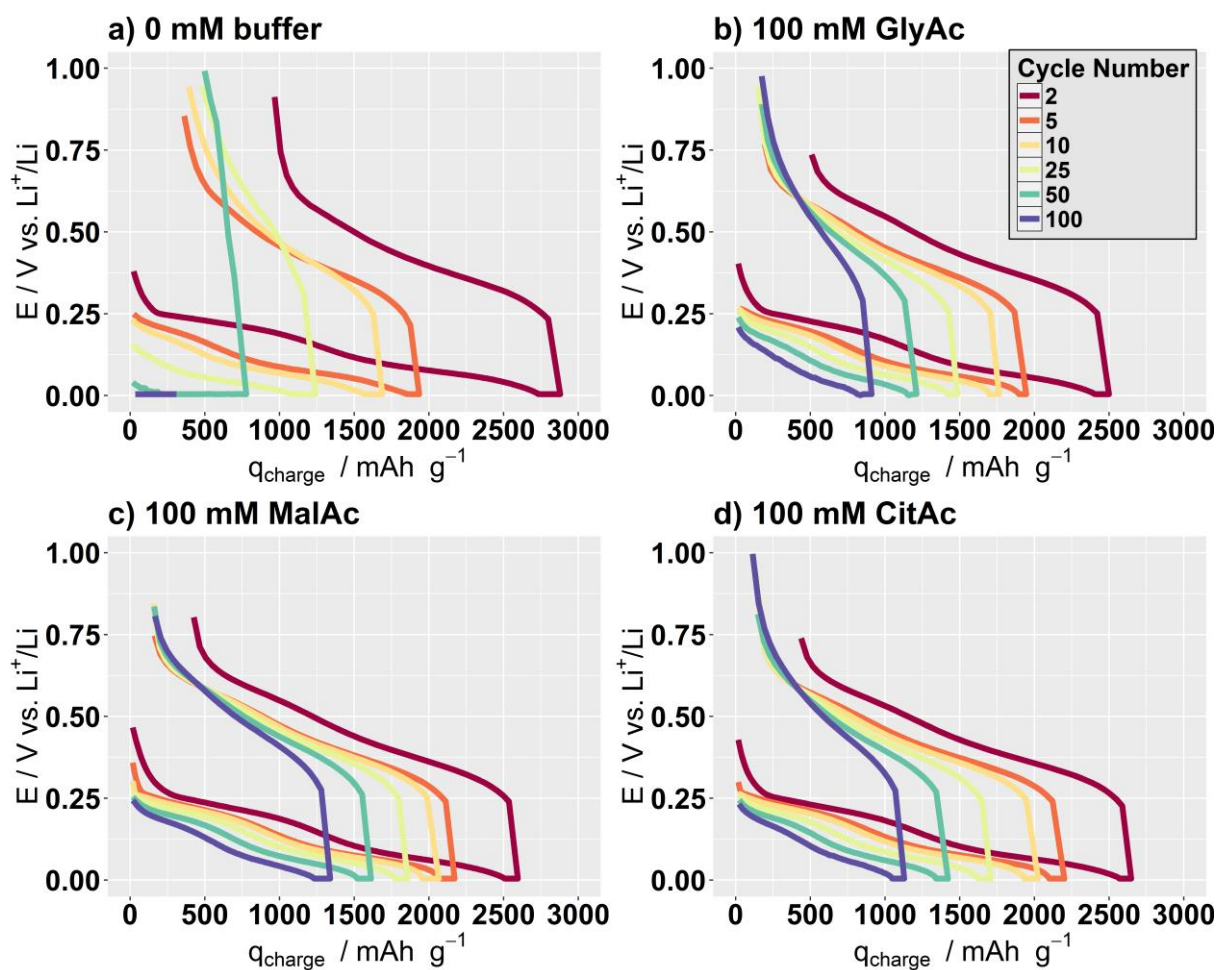


Figure S-12. Voltage profiles of the 3 carboxylic-acid-buffered electrode formulations and the unbuffered Si reference formulation for selected cycles.