Supporting Information

Polymer-Templated LiFePO₄/C Nanonetworks as High-Performance Cathode Materials for Lithium-Ion Batteries

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Figure S1: Size distributions of characteristic features of the BCP-micelle derived LFP morphology after low temperature annealing (Figure 1c), determined by analyzing TEM images similar to that of the inset in Figure 1e. The hollow structures have an average inner diameter of 28.5 ± 12.5 nm and an average outer diameter of 61.8 ± 20.3 nm. The average wall thickness corresponds to 16.6 ± 5.8 nm.



Figure S2: XRD patterns (without baseline correction) of the BCP-templated samples for two different heat treatments. Annealing at 700 °C in argon results in phase-pure crystalline LFP. Calcining the precursors at 500 °C however yields an amorphous phase with no distinct peaks. The LFP reference pattern is also shown for comparison.



Figure S3: (a,b) SEM and (c,d) TEM images of the (a,c) BCP-templated LFP/C and (b,d) nontemplated composites after annealing at 700 °C in argon. The BCP-templated structure possesses a uniform carbon-coating (c), whereas the nontemplated material exhibits extra carbon that is not in intimate contact with the active material (d). Scale bars: main images: 500 nm, insets: 100 nm.

Figure S4: High resolution TEM images of the BCP-templated LFP/C material. a) The composite shows a connected network of crystalline particles that are coated with a uniform carbon layer. b) The measured lattice spacing of approximately 0.36 nm corresponds to the (111) lattice planes of LiFePO₄. Scale bars: 10 nm.

Figure S5: Insufficient carbon-coating (due to lower BCP and/or homopolymer content) leads to uncontrolled crystal growth that can damage the mesostructure. a) SEM image showing the formation of some larger crystallites in a nanosized LFP/C network when using a BCP to homopolymer ratio of 4:5. b) SEM image showing the formation of large LFP crystallites at the top surface of a deposited BCP-templated LFP/C thin film. Scale bars: $1 \,\mu\text{m}$.

Figure S6: (a,b) Physisorption measurements for a) the BCP-templated LFP/C composite with a specific surface area of $38.2 \pm 1.0 \text{ m}^2/\text{g}$ and b) the nontemplated material with a specific surface area of $36.3 \pm 0.2 \text{ m}^2/\text{g}$, based on a Brunauer-Emmett-Teller (BET) analysis.¹ (c,d) Pore size distribution as determined by applying the Barrett-Joyner-Halenda (BJH) method² to the absorption branches of the c) BCP-templated and d) nontemplated materials. Note that both samples show a characteristic peak for pore sizes between 3 and 4 nm which can be attributed to mesopores in the carbon-coating. The nontemplated material shows a broad peak for pore sizes around 20 nm, corresponding to the structure of the extra carbon that is not in direct contact with the particle surface (Figure S3d). The BCP-templated pore size distribution shows an increase for feature sizes larger than approximately 30 nm which can be ascribed to pores and interparticle distances in the nanonetwork (Figure S3c).

Figure S7: a) SEM and b) TEM images of the precursor structure of the nontemplated material after solvent evaporation. The material was synthesized using the same sol-gel method but without the use of a BCP. It was calcined at 500 °C in air before imaging. Scale bars: a) 500 nm, b) 100 nm.

Figure S8: Carbon structure of the nontemplated LFP/C composite. a) Raman shift showing the D- and G-band of carbon with a peak area ratio (A_G/A_D) of approximately 0.41. b) TGA data performed in air showing the weight gain due to oxidation of LFP and the weight loss from burning off the carbon. The resulting carbon content of ~ 10.9% is comparable to the BCP-templated case.

Figure S9: Cyclic voltammetry at different scan rates for the BCP-templated LFP/C composite electrode showing single oxidation and reduction peaks.

Figure S10: Cycling rate dependence of charge and discharge overpotentials for BCPtemplated (blue circles) and nontemplated (red squares) samples. The data points were obtained by identifying the voltage plateaus of the charge and discharge processes at the respective cycling rates (cf. Figure 3). The first (dis)charge cycle was neglected in all cases. The associated curves are fits using the Butler-Volmer equation³ including an ohmic resistance (BV), the MHC model that describes the kinetics of electron transfer between the carbon-coating and the active material,⁴ and a phenomenological model that comprises a logarithmic and a linear relationship between voltage and current (LL). The fit parameters and details of the models are presented in Table S3 and the overpotential analysis section (see below), respectively.

| Sample | BCP-templated | Nontemplated | |
|--|------------------------|------------------------|--|
| Mass (mg) | 0.779 | 1.16 | |
| $L_{\rm Connection}$ (H) | 1.35×10^{-06} | 1.44×10^{-06} | |
| $R_{\text{Connection}}(\Omega)$ | 6.51 | 5.35 | |
| $R_{ m Lithium} (\Omega)$ | 12.4 | 8.29 | |
| C_{Lithium} (F) | 1.80×10^{-05} | 9.54×10^{-05} | |
| $R_{\text{Electrode}} (\Omega)$ | 17.3 | 70.4 | |
| $Q_{\text{Electrode}}$ (S s ⁿ) | 5.70×10^{-05} | 8.69×10^{-05} | |
| $n_{\rm Electrode}$ | 66.8 | 61.9 | |
| $Q_{\text{Diffusion}}$ (S s ⁿ) | 1.54×10^{-02} | 2.73×10^{-02} | |
| $n_{\rm Diffusion}$ | 0.518 | 0.344 | |

Table S1: Fit parameters for EIS data (Figure 3b) according to the equivalent circuit model shown in the inset (not normalized by electrode mass).

Table S2: Fit parameters for EIS data (Figure 3b) according to the equivalent circuit model shown in the inset (normalized by electrode mass).

| Sample | BCP-templated | Nontemplated | |
|--|------------------------|------------------------|--|
| Mass (mg) | 0.779 | 1.16 | |
| $L_{\rm Connection}$ (H g) | 1.05×10^{-09} | 1.68×10^{-09} | |
| $R_{\text{Connection}} (\Omega \text{ g})$ | 5.07×10^{-03} | 6.22×10^{-03} | |
| $R_{\text{Lithium}} (\Omega \text{ g})$ | 9.64×10^{-03} | 9.63×10^{-03} | |
| $C_{ m Lithium}~({ m F/g})$ | 2.31×10^{-02} | 8.21×10^{-02} | |
| $R_{\text{Electrode}} (\Omega \text{ g})$ | 1.35×10^{-02} | 8.18×10^{-02} | |
| $Q_{ m Electrode} ({ m S~s}^n/{ m g})$ | 7.31×10^{-02} | 7.48×10^{-02} | |
| $n_{\rm Electrode}$ | 0.668 | 0.619 | |
| $Q_{ m Diffusion}~{ m (S~s^n/g)}$ | 19.8 | 23.5 | |
| $n_{\text{Diffusion}}$ | 0.518 | 0.344 | |

Overpotential analysis

We use a model that employs the Butler-Volmer equation³ and an ohmic resistance term (BV) to express the (mass-normalized) current I (described by the C-Rate) and the (plateau) potential V in terms of the charge transfer overpotential η_{ct} . The current reads $I = I_0^{BV} [\exp(-\alpha \eta_{ct}) - \exp((1-\alpha) \eta_{ct})]$ and the potential is given by $V = (\eta_{ct} + R^{BV} I)/f + V_0^{BV}$. I_0^{BV} is the exchange current, R^{BV} the ohmic resistance and V_0^{BV} the equilibrium potential. The charge transfer coefficient was assumed to be $\alpha = 0.5$ and $f = e/k_BT = 1/25.7 \text{ mV}$. The

Table S3: Fit parameters for different models that describe the relationship between the plateau potential of the charge / discharge curves and the applied C-rate (units of 1/h) for the BCP-templated and the nontemplated samples (cf. Figure S10). The models and fits are discussed in the overpotential analysis section.

| Sample | BCP-templated | | Nontemplated | |
|-------------------------------------|---------------|--------|--------------|--------|
| Mass (mg) | 0.779 | | 1.16 | |
| | Discharge | Charge | Discharge | Charge |
| $I_0^{ m BV}$ (1/h) | -12.6 | -3.15 | -2.97 | -0.910 |
| $R^{\rm BV} \ ({\rm mV} \ {\rm h})$ | 7.94 | 7.90 | 7.93 | 7.43 |
| $V_0^{\rm BV}$ (V) | 3.40 | 3.45 | 3.40 | 3.45 |
| $A^{ m MHC}$ (1/h) | -3.41 | -2.92 | -2.84 | -2.52 |
| $\lambda^{ m MHC}$ | 5.5 | 6 | 7 | 9 |
| $V_0^{\rm MHC}$ (V) | 3.40 | 3.45 | 3.39 | 3.45 |
| $A^{\rm LL} \ ({\rm mV})$ | -1.61 | 2.43 | -7.23 | 15.7 |
| $R^{\rm LL} \ ({\rm mV \ h})$ | 9.18 | 11.7 | 10.5 | 11.7 |
| $C^{\mathrm{LL}}(\mathrm{V})$ | 3.40 | 3.46 | 3.38 | 3.49 |
| SOC (% of Q_{theo}) | 4 | 8.5 | 3 | 8 |

Butler-Volmer equation describes the charge transfer of lithium ions from the liquid electrolyte to the active material. The nontemplated material shows a larger overpotential due to these charge transfer related phenomena, which correlate to its coarser mesostructure compared to the BCP-templated case.

It has however been suggested that charge transfer in LFP electrodes is not limited by the transfer of ions but by the transfer of electrons from the conductive carbon to the active material.⁴ The MHC model quantifies the kinetics of the electron transfer process. In this case the current is given by

 $I = A^{\text{MHC}} \left[\int_{-\infty}^{\infty} \exp\left\{ -\frac{(x-\lambda^{\text{MHC}}+\eta_{\text{ct}})^2}{4\lambda^{\text{MHC}}} \right\} \frac{\mathrm{d}x}{1+\exp(x)} - \int_{-\infty}^{\infty} \exp\left\{ -\frac{(x-\lambda^{\text{MHC}}-\eta_{\text{ct}})^2}{4\lambda^{\text{MHC}}} \right\} \frac{\mathrm{d}x}{1+\exp(x)} \right].$ If ohmic contributions are neglected, the potential is given by $V = \eta_{\text{ct}}/f + V_0^{\text{MHC}}$. A^{MHC} is the pre-exponential factor (accounting for the electronic coupling strength and the electronic density of states of the electrode), λ^{MHC} is the dimensionless reorganization energy (scaled to $k_{\text{B}}T$) and V_0^{MHC} is the equilibrium potential. The nontemplated material shows larger reorganization energies and smaller pre-exponential factors. Finally, we point out that the overpotential behavior can also be modeled by a simple, phenomenological model (LL), $V = A^{\text{LL}} \ln |I| + R^{\text{LL}} I + C^{\text{LL}}$. The fit parameter A^{LL} is the prefactor of the logarithmic term. R^{LL} labels the pre-factor of the linear term (equivalent to an ohmic resistance) and $C^{\text{LL}} = V_0^{\text{LL}} - A \ln(I_0^{\text{LL}})$ is a constant combining voltage contributions from the equilibrium potential V_0^{LL} and the exchange current I_0^{LL} (in analogy to the Butler-Volmer equation). The logarithmic overpotential contribution is significantly higher in the nontemplated case.

Note that equilibrium potentials for charge and discharge were independently determined and can differ due to the many-particle nature of the composite electrode.⁵ The voltage values were taken at the state of charge or discharge (SOCs) at which the voltage profile first assumes a constant (plateau) voltage. The fit parameters for the described models and the respective SOCs (in percentage of the theoretical capacity of the electrode, Q_{theo}) are given in Table S3.

References

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