Journal Name

RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received ooth January 2012, Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

ESI[†]: Li- and Na-Reduction Products of *meso*-Co₃O₄ form high-rate, stably cycling battery anode materials

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High surface area (367 m² g⁻¹) meso-porous Co₃O₄ was investigated as the precursor of the anode material for lithium and also sodium ion batteries. Co_3O_4 is considered a potential anode material due to its theoretical capacity of 890 mAh g⁻¹, over twice that of graphite This comparatively higher capacity can be safely charged at rapid rates owing to a relatively high Li-insertion potentials, but, consequently, the discharged energy is yielded at an average potential near 2 V vs Li/Li⁺, with full Li-extraction achieved over a continuum of potentials up to 3 V. The products of the lithium reduction of Co_3O_4 cycle stably from 0.01 - 3.0 V vs Li/Li⁺ with 600-900 mAh/g capacity retention at C rates from 1-5; the products of its sodium reduction cycle stably from 0.01 - 3.0 V vs Na/Na⁺ at C-rates up to 1C with a lower 150-400 mAh/g capacity retention owing to greater ionic impedance. TEM, SAED and XRD were used to examine the cycled material and the stable performance is attributed to finding that the mesoporous structure is retained. Evaluation of five electrolyte formulations testing EC, FEC and Cl-EC showed that the stable meso-porous structure was best cycled with 5% FEC in EC:DEC at high charge/discharge rates, retaining 77% of its initial capacity at 5C in a rate test.Comparison of the AC impedance spectra and of the XPS of the SEIs formed in the presence and in the absence of 5 vol. % FEC shows that the SEI formed in the presence of FEC contains lithium fluoride and its carbonate layer is thinner than that formed in its absence, resulting in lesser impedance to Li migration through the SEI and facile ion de-solvation, improving the cycling performance. In cycling stability tests with EC:DEC, irregular cycling behaviour attributable to abrupt rises in cell resistance was regularly observed after testing over a few hundred cycles. Long-term cycling irregularities are inhibited by halogenated solvents and completely eliminated by adding fluoroethylene carbonate (FEC).

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1. SEM of un-cycled electrode



Fig. S1a. SEM cross-sectional image of un-cycled meso-porous Co₃O₄ based electrode on copper foil current collector.



Fig. S1b. SEM cross-sectional image of un-cycled meso-porous Co₃O₄ based electrode showing meso-porous material surrounded by Super-P Li conductive additive.

1. X-ray photoelectron spectroscopy (XPS) characterization and analysis procedure

XPS analysis of SEI surface of cycled electrodes

The peak assignments for the XPS spectra were described in the experimental section. The peak assignments used for analysing the spectra of SEI formed upon lithium ion anodes are summarized in the tables below. Our interpretation of the data is that it represents the surface of a SEI which extends beyond the depth of characterization for XPS (estimated to be ~ 10 nm) because no cobalt signal was observed.

Region	Species	Binding Energy (eV)	Ref.	Binding energy tolerance (eV)	FWHM Range (eV)	Lineshape
C 1s	sp ² C in graphitic C	282.5	1	282.5±0.25	0 - 2	GL(30)
	С-Н, С-С	284.5	1	284.5±0.1	0 - 2	GL(30)
	alkyl and alkoxy carbons	285-287	2	286±0.25	0 - 3	GL(30)
	ethereal, alkoxy carbon	286-288	2	287±0.25	0 - 3	GL(30)
	R- <u>C</u> H ₂ -OCO ₂ -Li	287.7-288.2	3	288±0.25	0 - 2	GL(30)
	R-CH ₂ -O <u>C</u> O ₂ -Li	289.2-290.2	3	289.5±0.25	0 - 2	GL(30)
	Li ₂ CO ₃	290.5-291.5	4	291±0.25	0 - 3	GL(30)
O 1s	LiOH	531	2, 5	530.8±0.25	0 - 2.5	GL(30)
	ROCO2Li / Li2CO3	532	6	531.8±0.25	0 - 2.5	GL(30)
	R <u>O</u> CO ₂ Li	533	6	533.2±0.25	0 - 2.5	GL(30)
	ROLi	534	6	534.5±0.25	0 - 2.5	GL(30)
Li 1s	LiF	56	2	not fitted		
	Li ₂ CO ₃	55.5	2	not fitted		
	alkoxide, hydroxide Li-O	55.5	2	not fitted		
	Li ₂ O	54	2	not fitted		
F 1s	LiF	685	2	685±0.25	0 - 2	GL(30)
	P-F, CF ₂	687.2-687.7	1	687.2±0.25*	0 - 3	GL(30)
				*±0.5 for Cl-EC ba	sed electrolytes	
Р 2р	LiPF ₆	138	3	not fitted		
Cl 2p	LiCl	198.5-6	7	not fitted		GL(30)
	CH3Cl	200.8	8	not fitted		GL(30)

Tab	le S1a.	Regiona	l assignments	for s	pecies	constituting	the L	i-ion de	rived S	SEIs.

The peak assignments for Na-ion derived SEI were similarly aligned and assigned.

Table S1	b. Regional	assignments for	· species	constituting th	e Ni-ion	derived SEIs.
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Region	Species	Binding Energy (eV)	Ref.	Binding energy tolerance (eV)	FWHM Range (eV)	Lineshape
C 1s	sp ² C in graphitic C	282.5	1	282.5±0.25	0 - 2	GL(30)
	С-Н, С-С	284.5	1	284.5±0.1	0 - 2	GL(30)
	alkyl and alkoxy carbons	285-287	2	286±0.25	0 - 3	GL(30)
	ethereal, alkoxy carbon	286-288	2	287±0.25	0 - 3	GL(30)
	R- <u>C</u> H ₂ -OCO ₂ -Na	287.7-288.2	3	288±0.25	0 - 2	GL(30)
	R-CH ₂ -O <u>C</u> O ₂ -Na	289.2-290.2	3	289.5±0.25	0 - 2	GL(30)
	Na ₂ CO ₃	290.5-291.5	4	291±0.25	0 - 3	GL(30)
O 1s	NaOH	531		531±0.25	0 - 2.5	GL(30)
	Na ₂ CO ₃	532	6	532±0.25	0 - 2.5	GL(30)
	ROC <u>O</u> 2Na	533	6	533±0.25	0 - 2.5	GL(30)
	R <u>O</u> CO ₂ Na/RONa	534	6	534±0.25	0 - 2.5	GL(30)
	Na KLL Auger	536	9	536±0.25	0 - 3	GL(30)
Na 1s	NaF	1071-1072.5	10,11	not fitted		
F 1s	NaF	686.6	12, 2	685.7±0.25	0 - 3	GL(30)
	PF6-	688.8	12	687.9±0.25	0 - 3	GL(30)
	C-F	691	12	687.9±0.25	0 - 3	GL(30)

Evaluation of the meso-porous Co₃O₄ particle

A 250 cycle test at 1C was conducted in with nominally identical electrodes tested in alternative electrolyte formulations. The slight aberration in cycling results and coulombic efficiencies at cycle 200 is due to the cell being stopped and restarted.



Fig. S2. 250 cycle test in lithium-ion cell at 1C after conditioning cycle at C/20 for nominally identical electrodes cycled in 5 different electrolyte formulations (indicated in legend).



Fig. S3a. TEM at 2 magnifications of (ultramicrotomed) sections of electrode in fully discharged state after 250 cycles testing at 1C rate. The *meso*-porous channels are observed to remain intact. Here, electrodes cycled in 1M LiPF₆ in EC:DEC, 5% FEC in EC:DEC or FEC:DEC shown.



Fig. S3b. TEM at 2 magnifications of (ultramicrotomed) sections of electrode in fully discharged state after 250 cycles testing at 1C rate. The *meso*-porous channels are observed to remain intact. Here, electrodes cycled in 1M LiPF₆ in 5% Cl-EC in EC:DEC or Cl-EC:DEC shown.



Fig. S3c. TEM of (ultramicrotomed) sections of un-cycled electrode showing (a) wide-field view of electrode and copper foil current collector (black, top right corner) and (b) *meso*-porous particle with channels in plane of view.



Fig. S3d. TEM of (ultramicrotomed) section of electrode in fully discharged state after 250 cycles at 1C rate in 1 M LiPF₆ in 5% FEC in EC:DEC electrolyte formulation. The material in this frame appears to be structured in a manner unlike the anticipated *meso*-porous arrangement and was observed in only a few locations during the several hours of TEM characterization performed. This structure is not considered representative of the bulk of the *meso*-porous particles as it was observed in only a very small fraction of the electrode. Based upon consideration of the many images taken during TEM and SEM characterization, we suggest that this structure may be possibly explained by: (i) a small fraction of the synthesized *meso*-porous Co₃O₄ material forming nanorod clusters, (ii) the *meso*-porous channels being largely filled as a result of the active material swelling as it experienced volumetric changes during charge and discharge or (iii) that the channel walls "ball-up" into what appears to be a string of beads when the particle is cut at a particular, transverse angle (during ultramicrotoming).



Fig. S4. XRD of cycled electrode in discharged state after 500 cycles at 1*C* in lithium ion cell with 5% FEC in EC:DEC electrolyte formulation. The peaks observed are due to the copper substrate of the electrode and the splitting is a result of the difference in the k-alpha 1 and k-alpha 2 Cu energies. Inset on the Fig. are comparisons of higher resolution diffraction patterns obtained from selected 2-theta domains, comparing the signal electrode to a pristine piece of the copper foil current collector. Patterns taken on similarly cycled anode material removed from the Cu current collector showed no features, confirming the result shown here.



Fig. S5a,b. (a) SAED pattern and (b) corresponding particle with amorphous structure.



Fig. S5c,d. (a) SAED pattern and (b) corresponding particle with CoO structure indicated by six-fold symmetry along the 1 -1 1 zone axis.



Fig. S5e,f. SAED of electrode showing Co_3O_4 phase in discharged state after 250 cycles at 1*C* rate testing in 5% FEC in EC:DEC electrolyte. (c) the diffraction spots obtained for the material in (d) correspond to the Co_3O_4 phase: despite the few diffraction spots able to be recorded, the 0 2 2 ring is good evidence for the existence of this phase, for these diffraction spots are at a reciprocal distance far removed from that of any other cobalt oxide phase d-spacing.



Fig. S6a,b. (a) *in-situ* XRD pattern collected for the charge (*via* linear voltammetry) of an electrode composed of 80/10/10 nanopowder Co_3O_4 (Sigma, less than 50 nm), CMC_{90kDa} and Super-P Li in a modified 2032 coin cell. The test was conducted using Phillips X'PERT scanning 35-46 degrees 20 with 2.5 second dwell on 0.05 degree 20 step size. (b) The linear voltammetry was conducted at 0.05 mV/s from 2.0 to 0.01 V and the start of each XRD scan is indicated by dotted lines. Similar testing done on the *meso*-porous electrodes were inconclusive, owing to very weak crystalline signal from the active material.

Table S2aCapacities and capacity retention for 1C rate test of Li-ion half cells through 500 cycles								
Electrolyte	C/20	1C, 500 th cycle	Max. 1C capacity	% retention of C/20 capacity, 1C 500 th cycle	% retention of max 1C	1st cycle CE	average CE at 1C	
EC:DEC*	816	925	843	113%	110%	65.8	99.3	
5% FEC in EC:DEC	736	673	800	91%	84%	67.7	99.1	
FEC:DEC	807	685	748	85%	92%	64.3	99.6	
5% Cl-EC in EC:DEC	808	752	845	93%	89%	62.9	99.3	
CIEC:DEC	762	n/a	730	n/a	n/a	50.0	n/a	

ble S2a	Capacities and ca	pacity retention	for 1C rate test	of Li-ion half ce	ls through 500 cycles

* irregular, repeated abrupt increases in cell resistance resulted in unstable cycling performance



Cycling test at 1C rate for 500 cycles following C/20 conditioning cycle in half cell of meso-porous Co₃O₄ based Fig. S7. electrodes vs Li-foil with 1M LiPF₆ in Cl-EC:DEC electrolyte formulation. The mass loading of the cell is reduced (0.45 mg cm⁻²) compared to the typical electrode tested in this study.



Fig. S8a. Voltage profile showing voltage spikes for cell tested in 1M LiPF₆ in EC:DEC for 500 cycle test at 1C rate.



Fig. S8b,c. Erratic cycling behaviour exhibited by *meso*-porous electrodes tested in 1M LiPF₆ in EC:DEC electrolyte during 1C test for 500 cycles indicating dendritic formations.



Fig. S9. Electrochemical data for the electrode tested in the 1M LiPF₆ in EC:DEC electrolyte for 500 cycles at 1*C* rate. (a), (c) differential capacity profiles and (b), (d) corresponding voltage profiles for the lithiation half-cycle grouped according to before and after the *ca*. 270th cycle, after which unusual cycling behaviour was observed (e.g. increasing capacity, unstable capacities and coulombic efficiencies).

	(capacity in	mAh/g at e	nd of rate	test series				
Electrolyte	C/20	C/10	1C	5C	5C (319 th cycle)	10C (519 th cycle)	5C (719 th cycles)	1C (800 th cycle)
EC:DEC	793	806	744	454	255	117	229	839
5% FEC in EC:DEC	817	861	820	631	558	209	492	941
FEC:DEC	703	721	636	490	435	153	367	634
5% Cl-EC in EC:DEC	790	818	745	454	418	165	286	518
CIEC:DEC	867	896	762	264	107	65	84	365

Table S3a. Capacities for C-rate test of Li-ion half cells through 800 cycles at variable rates

Table S3b.Capacity retention as percent of C/20 conditioning cycle for for C-rate test of Li-ion half cells through 800
cycles at variable rates

	(capacity in	mAh/g at e	nd of rate	test series				
Electrolyte	C/20	C/10	1C	5C	5C (319 th cycle)	10C (519 th cycle)	5C (719 th cycles)	1C (800 th cycle)
EC:DEC	100%	102%	94%	57%	32%	15%	29%	106%
5% FEC in EC:DEC	100%	105%	100%	77%	68%	26%	60%	115%
FEC:DEC	100%	103%	90%	70%	62%	22%	52%	90%
5% Cl-EC in EC:DEC	100%	104%	94%	57%	53%	21%	36%	66%
CIEC:DEC	100%	103%	88%	30%	12%	7%	10%	42%



Fig. S10. Cycling test of 80% meso-porous Co₃O₄ (1.0 mg/cm² loading) / 10% Super-P Li / 10% CMC_{90kDa} electrode in 1M LiPF₆ in 5% FEC in EC:DEC electrolyte. (a) Variable high rate test at 5*C*, 10*C* and 5*C* for 500 cycles each followed by 1*C*. (b) Cycling at 1*C* rate to different lower voltage cut-offs.



Fig. S11. (a) Equivalent circuit used to model AC impedance spectra. (b) Bar graph indicating contribution to resistance from each circuit resistor when cell is at state of full charge. (c) Bar graph indicating the magnitude of the diffusion term extracted from the Warburg impedance element for the electrode in its fully charged and discharged states.

 Table S4.
 AC impedance values given as percent of the resistance through each element of the spectra obtained for the electrode tested in the EC:DEC electrolyte

Electrolyte	R _{SEI} , 100 mV	R _{ct} , 100 mV	L^{2}/D , 100 mV	L ² /D, discharged
5% FEC in EC:DEC	64%	41%	83%	22%
FEC:DEC	150%	5%	172%	66%
5% Cl-EC in EC:DEC	115%	35%	81%	64%
CI-EC:DEC	353%	28%	609%	168%



Fig. S12. Cycling performance of lithium ion electrode tested through 1000 cycles at 1C in hybrid electrolyte of 1/1/2 volume percent Cl-EC/FEC/DEC. Electrode composition was 60 % meso-porous Co₃O₄, 20% Super-P Li and 20% PAA_{50kDa}.



Fig. S13. Species composition in the C 1s region for each of the SEIs derived from Li-ion half-cell testing with the 5 electrolytes evaluated.

Table S5. AC Impedance Table (Resistances for Na-ion cells) for electrodes at state of full charge in cycle 10 (C/20 rate testing)

Electrolyte	R_{SEI} , 100 mV (Ω)	R _{ct} , 100 mV (Ω)		
5% FEC in EC:DEC	7241 ± 132	3055 ± 208		
FEC:DEC	1367 ± 33	1510 ± 86		



Fig. S14. Species composition in the C 1s region for each of the SEIs derived from Na-ion half cell testing with the 2 electrolytes evaluated.

Discussion of differential capacity profiles

Li-ion cells

Differential capacity profiles illustrate the phase transitions and thereby indicate the mechanism by which the active material charges with and discharges lithium (or sodium). The peaks typically represent phase transitions or other reactions; depending on the kinetics of the reaction or phase transition, the potential of these peaks will occur at some overpotential beyond the theoretical energy of formation. The primary practical value of these profiles for this study is in their identification the majority of the discharge occurring at high potentials (average near 2 V) vs the Li/Li⁺ redox couple. By inspection of a capacity vs. cycle number plot, the electrode performance appears stable and has the advantages of relatively good retention of capacity at high rates. However, this capacity is discharged at relatively high potentials, meaning that the energy quality is low. As a consequence, there is limited application of this active material; for example, we believe that it is unlikely that cobalt oxide would be attractive for use in electric vehicles or power tools, because both technologies require high voltage batteries.

In the first cycle differential capacity profile, there are 5 observed features during charge, the first of which (between 1.7 - 2.0 V) represents part of the charge which is irreversibly lost to SEI formation (labeled I in Fig. S12a ESI[†]). For the electrolytes containing Cl-EC, the SEI formation begins above 2 V and appears to further develop in a second reaction near 1.3 V while for the electrolytes containing FEC the SEI formation begins nearer 1.7 V. Initial SEI formation from the EC:DEC electrolyte also appeared to begin near 1.7 V. The charging of the Co_3O_4 is observed to occur at near 1.2 V (labeled II in Fig. S12a ESI[†]), this voltage being previously reported as the potential at which the mixed valence cobalt oxide forms Li₂O and CoO (Li_xCo₃O₄ has been reported, but only for very slow charge rates).¹³ The magnitude of this feature is difficult to determine because it appears to be convoluted (particularly in the case of the electrodes tested with an electrolyte containing Cl-EC) with an irreversible feature that possibly signifies a second phase of development of the SEI simultaneously as the Co_3O_4 matrix is distorted and its volume marginally increases.

At near 1.1 V, a two phase reaction occurs (labeled III in Fig. S12a ESI[†]); the corresponding chemistry may follow the traditionally accepted reaction pathway in which CoO is further reduced to Co metal in a matrix of lithia, but the accumulated charge after this feature (at 0.9 V) is only around 650-700 mAh/g, not nearly the theoretical capacity. Although more difficult to isolate, there is another feature (labeled IV in Fig. S12a ESI[†]) which would likely be ascribed to the reaction of lithium and the active material at near 0.7 V before a final and large feature (labeled V in Fig. S12a ESI[†]) appears, beginning at near 0.5 V. This large feature, V, represents almost exactly 1/3 of the entire capacity charged during this initial conditioning cycle. Feature V might represent the potential at which the bulk of the irreversible reactions occur (the irreversible capacities for the electrodes are near 500 mAh/g), the charging of the polymer gel often cited as a reason for why some cobalt oxide electrodes have higher than expected capacities¹⁴, the continuation of the lithiation of the active material or some combination of these.

Upon consideration of the contribution of this same feature to the charge capacity in subsequent cycling, we believe that feature V in the conditioning cycle marks the potential at which approximately half of the irreversible losses occur. This is estimated by evaluating the difference in capacities of (a) the extent of the contribution of feature V to the reversible capacity in cycle 100 (between 140-200 mAh/g or near 20% of the reversible capacity) and (b) the capacity of feature V in the conditioning cycle (between 350-425 mAh/g or nearly 33% of the reversible capacity). A small portion of the reversible storage of lithium accomplished in this low potential results is weakly held and readily discharges, signified by the linear portion of the discharge profile commencing at 70 mV and continuing up through about 1.0 V. At near 1.5 V, a slight feature is observed, perhaps corresponding to the phase transition during charge denoted as feature IV. Then, at near 2.0 V the majority of the discharge occurs; feature VIII, assigned to represent the delithiation of the lithia and the reformation of a mixture of CoO and Co_3O_4 (as observed by SAED), estimated to begin at about 1.75 V, accounts for about 55% of the reversible capacity in each electrode/electrolyte combination. As a practical consequence of the majority of the discharge chemistry occurring at these relatively high potentials,

the quality of energy delivered by a hypothetical future battery implementing a cobalt-oxide based anode would necessarily be low.

In the 1C testing done after the conditioning cycle, the differential capacity profile indicates the existence of a multi-step mechanism beyond the commonly accepted direct transition between a charged phase of lithia surrounding cobalt metal nanoparticles and a mixture of cobalt oxides in the discharged state. There is a small charge accomplished at a high potential of near 2.2 V before two features in sequence are observed at 1.4 V and 0.85 V. Similar to the profile from the conditioning charge, an incomplete feature begins at a low potential (shifted slightly, attributable to greater overpotential required for charging at the faster rate of 1 C). Because this feature does not present as a peak, even at low charge rates for which kinetics should not prevent the full lithiation of the material, we believe this feature does not represent a phase transition but, instead, an accumulation of charge possibly in the polymer as has been suggested previously.¹⁴ However, it is difficult to accurately interpret these differential capacity profiles, particularly with an incomplete understanding of the nature of phase transitions occurring at the lower potentials of charge. *In-situ* XRD has been employed by Larcher et al.¹³ but this technique only allows for analysis of the initial charging of Co_3O_4 . SAED analysis has indicated the formation of Co nanoparticles^{15,16} but this technique is inherently limited due to the small length scale of characterization. A technique such as Raman, capable of assessing the bonding of elements so as to clarify the extent of the degradation of the original mixed valence cobalt oxide structure, may help clarify the condition of the electrode at higher states of charge.

By the 500th cycle of 1 C testing, a difference is observed in the shapes of the differential capacity profiles (Fig. S13 ESI[†]), with a greater proportion of the discharge occurring in the discharge feature at near 1.5 V *vs* at 2.2 V (except, interestingly, in the case of the electrode cycled in 5% FEC in EC:DEC). The loss in capacity for the electrodes not forming dendrites (the electrode cycled in EC:DEC showed signs of dendritic growths in several cycles after about cycle 300) may be attributed to the attenuation of this feature, originally representing the potential at which most of the de-lithiation occurred.

When comparing the differential capacity profiles at variable *C*-rates (Fig. S14 ESI[†]), the effect of internal cell resistance becomes apparent, as the features in the profile are decreased, although not significantly shifted. For example, the increase in rate from 2 *C* to 5 *C* (cycle 69 vs cycle 89) results in an approximate increase of 100 mV in overpotential required to reach the two dominate features in charging. In the case of a silicon electrode, this increase in rate would more significantly shift the potentials at which the charge chemistry occurred, resulting in lower capacity as a consequence of the poor kinetics associated with the charge reaction.¹⁷ Here, this shift is not seen, although the lower capacity is evident, particularly for the electrodes tested in electrolyte formulations besides 5% FEC in EC:DEC. From this, we believe that the reason for lower capacity is linked to increased cell resistance attributable to issues arising from ion transport during charge transfer and transport across the electrode/electrolyte interface. As this interface thickness increases, the attenuation of the charge and discharge features similarly increases (differential profile for cycle 700 at 5 *C* in Fig. S14 ESI[†]). However, when the rate is lowered (to 1 *C*, Fig. S14 ESI[†]), the SEI and/or charge transfer steps are no longer limiting and full capacity is achieved in the case of the electrodes tested in 5% FEC in EC:DEC, FEC:DEC and EC:DEC.



Fig. S15. (a) Differential capacity profile for Li-ion half cells for conditioning cycle (carried out at *C*/20) rate before 500 cycle test at 1*C* rate. (b) Focus on the discharge side of the profile with (c) and (d) indicating in detail the charge profile. Black line corresponds to EC:DEC electrolyte formulation, blue line to 5% FEC in EC:DEC, green line to FEC:DEC, purple line to 5% Cl-EC in EC:DEC and red line to Cl-EC:DEC.

cycle 1	full charge	full	irreversible	% capacity after 550 mV,	% discharge capacity after 1.75 V
	capacity	discharge	losses	charge	
		capacity			
EC:DEC	1205	816	389	34%	56%
5% FEC	1087	736	351	32%	55%
FEC	1255	807	448	32%	56%
5% CIEC	1285	808	477	32%	57%
CIEC	1313	750	563	32%	55%

Table S6a. Significant values for differential capacity profiles of the conditioning cycle for Li-ion half cells.

 Table S6b. Significant values for differential capacity profiles of the 100th cycle (at 1C rate) for Li-ion half cells following the conditioning cycle described in S Table 6a.

cycle 100	full charge	full discharge capacity	irreversible losses	% capacity after 350 mV,
	capacity			charge
EC:DEC	851	840	11	23%
5% FEC	787	777	10	24%
FEC	743	740	3	19%
5% CIEC	845	836	9	23%
CIEC	673	670	3	21%



Fig. S16. (a) Differential capacity profiles at cycles 0 (conditioning cycle), 100 and 500 for Li-ion half cells tested at 1*C* rate after *C*/20 conditioning cycle. (b) Profile only of discharge for cycles shown in (a). Black line corresponds to EC:DEC electrolyte formulation, blue line to 5% FEC in EC:DEC, green line to FEC:DEC, purple line to 5% Cl-EC in EC:DEC and red line to Cl-EC:DEC.



Fig. S17. Differential capacity profiles at selected cycles during extended *C*-rate test. Black line corresponds to EC:DEC electrolyte formulation, blue line to 5% FEC in EC:DEC, green line to FEC:DEC, purple line to 5% Cl-EC in EC:DEC and red line to Cl-EC:DEC.

Na-ion cells

Partly as a consequence of the potential difference between the Li/Li⁺ and Na/Na⁺ redox couples (-3.04 V vs -2.714 V, respectively) and the free energy of formation of Li₂O and Na₂O, the charging and discharging of the Na-ion meso-porous Co_3O_4 half-cell proceeds at lower potentials than for the analogous reaction with Li: for the more stably performing electrode tested in FEC:DEC, the average potential of charge (cycle 100, 0.5 *C* rate) is 550 mV and the average potential of discharge is 1.58 V. By comparison, after 100 cycles at 1 *C* rate in FEC:DEC electrolyte in the lithium-ion cell, the average potentials of charge/discharge are 900 mV/1.76 V. Like with the lithium-ion cell, there are two dominant features in the (post conditioning cycle) differential charge profile for the Na-ion cell (Fig. S15 ESI[†]) followed by an incomplete feature which might be attributable to charge storage in the polymer gel layer at low potentials. The multiple (three discernable) discharge features likewise coincide with what was observed for the lithium-ion cells. However, in the Na-ion cell, there is no high voltage feature such as what is found near 2.2 V (charge) for the lithium ion cell (Fig. S14 ESI[†]).



Fig. S18. Differential capacity profiles at selected cycles during 250 cycle 0.5*C* test for Na-ion cells. Blue line corresponds to 5% FEC in EC:DEC electrolyte formulation, green line to FEC:DEC. (a) conditioning cycle at 0.025 *C*, (b) cycle 100 at 0.5 *C* and (c) cycle 200 at 0.5 *C*.

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