# A layer-structured $Na_2CoP_2O_7$ pyrophosphate cathode for sodium-ion batteries

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## Material Synthesis:

The $Na_2CoP_2O_7$ cathode compound was prepared by conventional one-step solid-state method, using a 2:1 molar mixture of $NaH_2PO_4$ (Wako, 99%) and $CoC_2O_4$ (Junsei, 99%) precursors. These components were mixed by planetary ball-milling for 1 h (400 rpm) dispersed in acetone media. For ball-milling, Cr-hardened stainless steel (Cr-SS) milling media and container were used. The remaining acetone was evaporated in vacuum to obtain the dried precursor mixture. It was ground, pelletized and fired at 600 °C for 6 h in a tubular furnace (with steady Ar flow) to obtain the final cathode material. In an alternate method, $Na_2CoP_2O_7$ was prepared by a splash combustion synthesis using stoichiometric amount of $NaH_2PO_4$ and $Co(NO_3)_3.6H_2O$ (Wako, 99%) along with citric acid ($C_6H_8O_7$, Wako, 98%) combustion agent, involving the final annealing at 600 °C for 1-6 h. Chemical desodiation was performed via chemical oxidation using $NO_2BF_4$ (Alfa Aesor, 96%) oxidizing agent dissolved in acetonitrile solvent (Wako, $H_2O$ level < 5 ppm). The solution containing $Na_2CoP_2O_7$ and $NO_2BF_4$ was stirred overnight (with steady argon bubbling) and the final product ($Na_{2-x}CoP_2O_7$) was filtered and dried at 60 °C. The chemical desodiation reaction can be written as:

$$Na_2CoP_2O_7 + NO_2BF_4 \rightarrow Na_{2-x}CoP_2O_7 + x\ NaBF_4 + (1-x)\ NO_2BF_4 + x\ NO_2\uparrow$$

## Structural and Physical Characterization:

X-ray diffraction patterns of $Na_{2-x}CoP_2O_7$ compounds were collected in the $2\theta$ range of 10-90° (with the speed of $1°.min^{-1}$) by using a Bruker AXS D8 ADVANCE diffractometer (operating at 35 mA, 40 kV) equipped with a Co-K$\alpha$ source ($\lambda_1$ = 1.78897 Å, $\lambda_2$ = 1.7929 Å) and a Vantec-1 linear position sensitive detector. Rietveld refinement was performed using TOPAS-Academic Ver. 4.1.[1] The crystal structures were drawn using the VESTA software.[2] Scanning electron micrographs were taken on combustion synthesized $Na_2CoP_2O_7$ powder sample mounted on conducting carbon paste using a Hitachi S-4800 SEM unit operating at 2 kV. Elemental analysis of $Na_{2-x}CoP_2O_7$ compositions were carried out with a Carl Zeiss SUPRA 40 SEM unit (operating at 15 kV) after washing the cycled cathode with propylene carbonate and drying at 25 °C. Infrared spectroscopy (FT-IR) was collected with a JASCO FT/IT-6300 unit using KBr pellets containing powder sample in the wavelength range of 400-4000 $cm^{-1}$.

## Electrochemical Characterization:

For electrochemical measurements, the active cathode material was formulated by mixing combustion-synthesized $Na_2CoP_2O_7$ and carbon in w/w ratio of 70/30. The working electrode was prepared by mixing the active cathode with polyvinylidene difluoride (PVdF) in a 9:1 (w/w) ratio. This working electrode composite was pressed on an Al mesh working as the current collector, with an average cathode loading of 3 mg/cm$^2$. Coin cells were assembled inside an Ar-filled glove box by taking the cathode film as the working electrode, Na metal foils as counter electrode and 1 M $NaClO_4$ dissolved in 98:2 mixture of propylene carbonate (PC) and fluoroethylene carbonate (FEC) acting as electrolyte. Galvanostatic cycling was conducted in the voltage range 1.5~4.7 V at a rate of C/20 (at 25 °C).

For electrochemical measurements with Lithium counter electrode, the cathode composite was prepared using 70% $Na_2CoP_2O_7$, 20% carbon black (ECP) and 10% polyvinylidene difluoride (PVdF) binder in minimal amount of N-methylpyrrolidone (NMP) solvent. The slurry was pasted on an Al-foil current collector and dried overnight at 120 °C (under vacuum) to remove the residual NMP. The punched out cathode sheet was used to assemble CR2032-type coin cell with Li metal foil as counter electrode, polypropylene film separator soaked in 1 M $LiPF_6$ in EC:DEC (3:7 v/v) electrolyte. Galvanostatic charge-discharge cycling was conducted in the voltage range 1.5~4.5 V at a rate of C/20 (at 25 °C), with a constant voltage relaxation down to C/200 applied at 4.5 V.

## Structural Illustration:

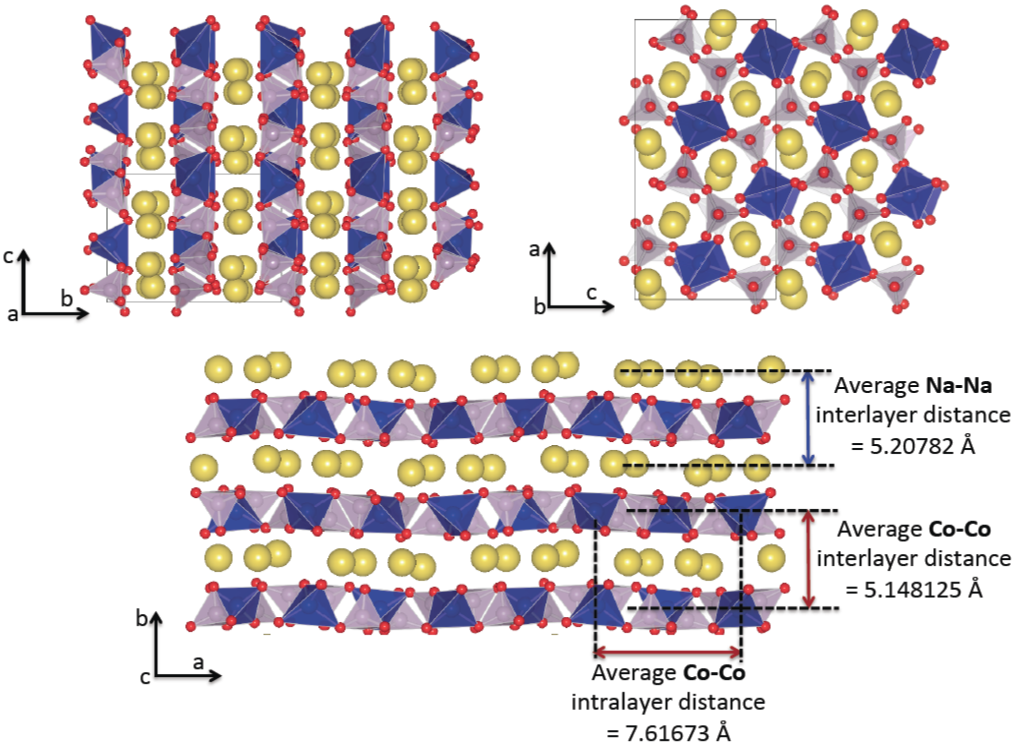


Figure S1: Structural illustrations showing the Na-diffusion channels in $Na_2CoP_2O_7$.

The crystal structure of $Na_2CoP_2O_7$ compound has been illustrated in Figure S1 along *a*, *b*, and *c* axis. Both the Na atoms and $CoO_4$-$PO_4$ $[Co(P_2O_7)^{-2}]$ units are arranged in a modulated fashion in the respective layers. Thus, both the intra-layer and inter-layer Na-Na and Co-Co interatomic distance varies slightly. Unlike many cathode materials, in case of $Na_2CoP_2O_7$, each Co-units (i.e. $CoO_4$) are separate from each other (no corner-sharing or edge-sharing) with the intra-layer Co-Co distance (7.61673 Å) being larger than inter-layer Co-Co distance (5.148125 Å). It offers two feasible channels for Na-ion diffusion along the *a* and *c* direction.

## Electrochemical analyses:

*(a) cycling stability*:

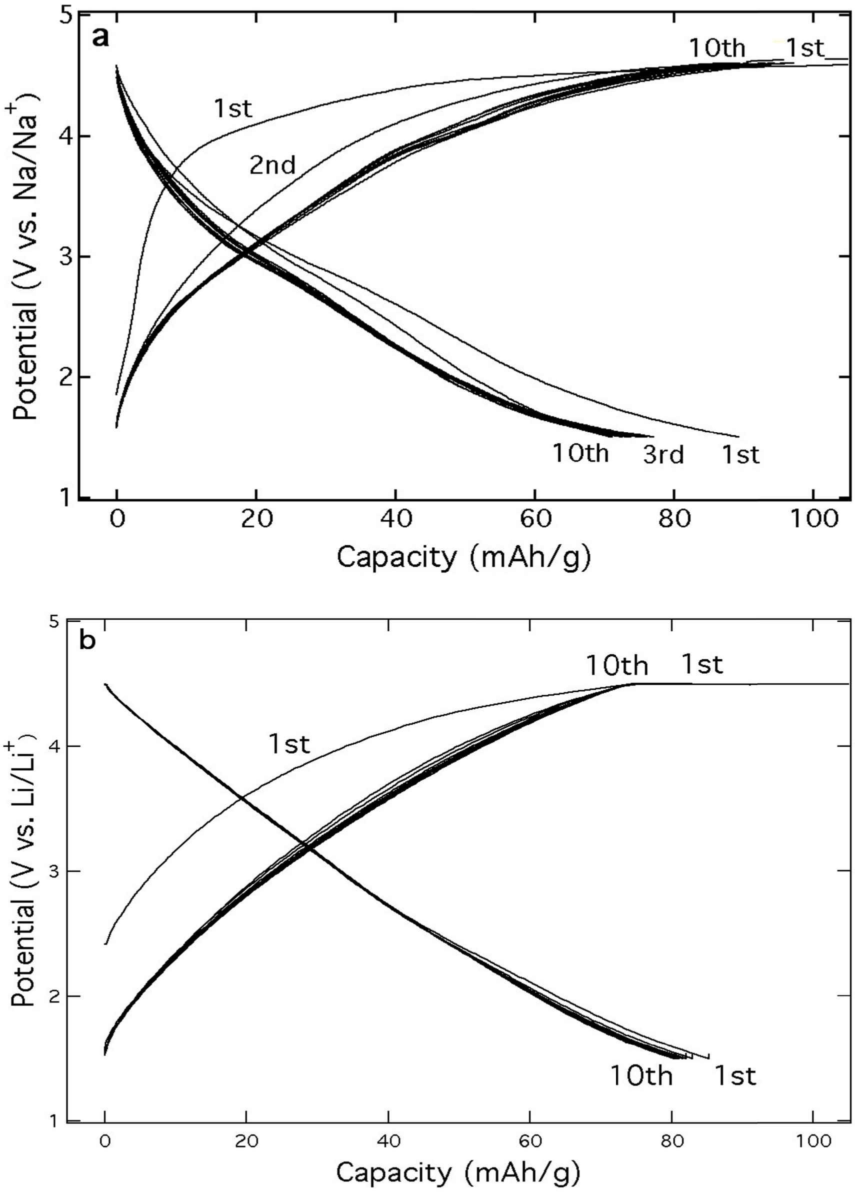


Figure S2a: Voltage drop between initial cycles of $Na_2CoP_2O_7$ cycled (top) vs. Na and (bottom) vs. Li.

There is a drop in (charge) voltage profiles from the 1st to subsequent cycles, both in Na and Li half-cell testing (Figure S2a). It can be due to the possible electrolyte decomposition and formation of SEI (solid electrolyte interface) during the first few cycles. After that, it stabilizes to develop reversible voltage-composition profiles.

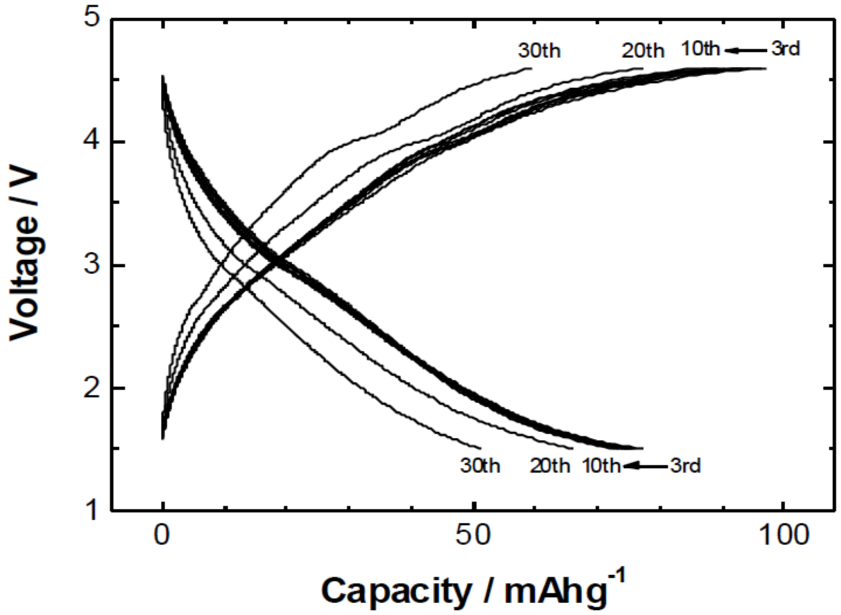


Figure S2b: Gradually fading cycling stability in $Na_2CoP_2O_7$ cathode.

Although $Na_2CoP_2O_7$ delivers excellent reversibility in the initial stage (up to 10 cycles), it slowly fades upon continuous cycling.

*(b) Galvanostatic cycling of pure carbon electrode:*

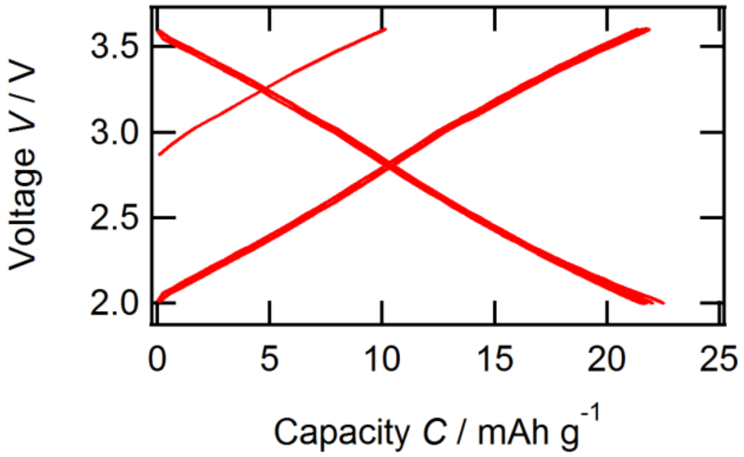
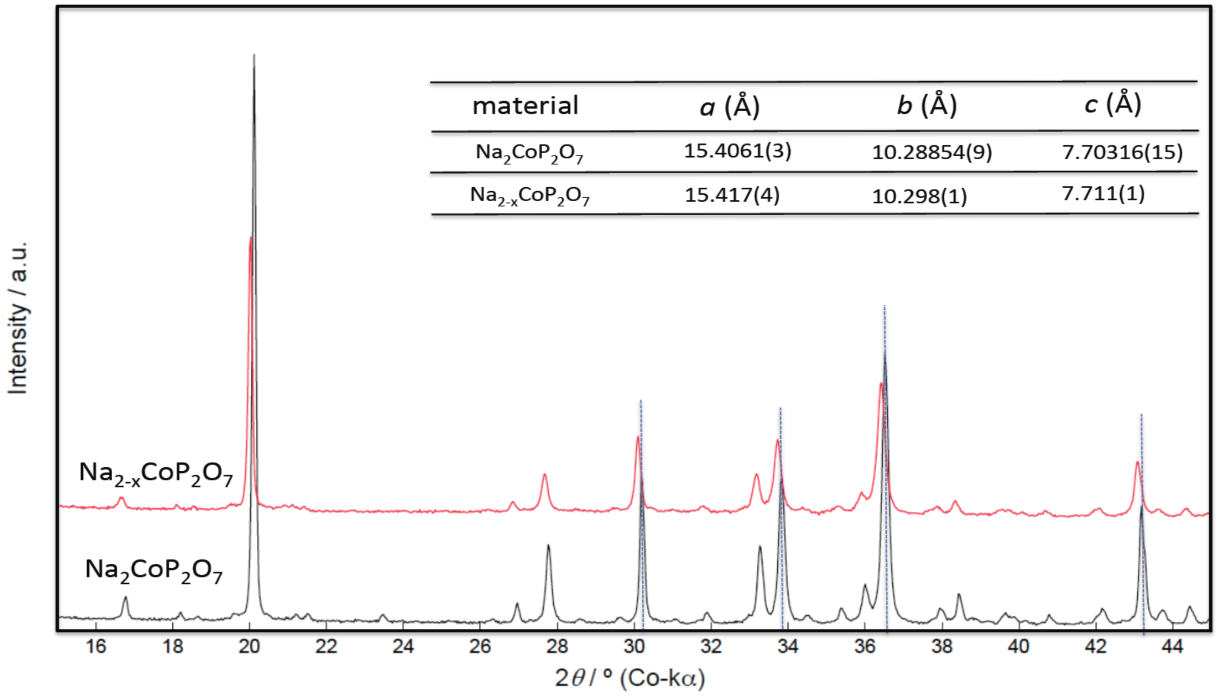


Figure S3: Voltage-composition curve of all-carbon cathode cycled vs Li. It delivers a maximum capacity of 22 mAh/g at an average voltage of 2.8 V (vs. Li) with excellent cycling stability over 200 cycles. It implies the capacity (approaching 80 mAh/g) in $Na_2CoP_2O_7$ cathode cannot be assigned solely to its carbon content in the cathode composite.

## Chemical desodiation analyses:



| material | *a* (Å) | *b* (Å) | *c* (Å) |
|---|---|---|---|
| $Na_2CoP_2O_7$ | 15.4061(3) | 10.28854(9) | 7.70316(15) |
| $Na_{2-x}CoP_2O_7$ | 15.417(4) | 10.298(1) | 7.711(1) |

Figure S4: Comparative X-ray patterns of pristine $Na_2CoP_2O_7$ and chemically oxidized $Na_{2-x}CoP_2O_7$. The desodiation process leads to slight peak shifting towards lower angle hinting at possible lattice expansion.

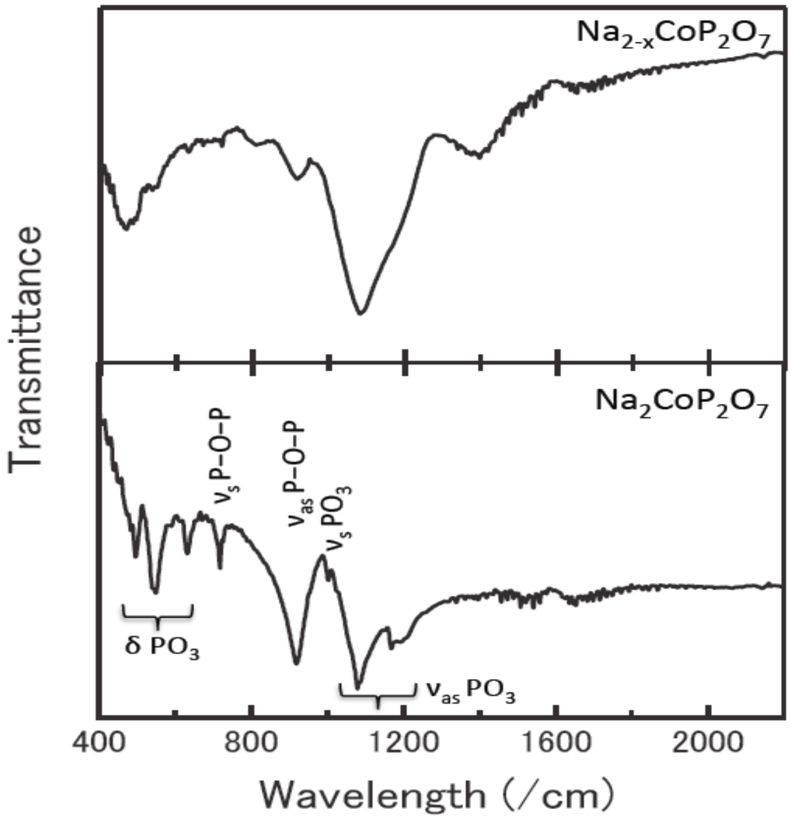
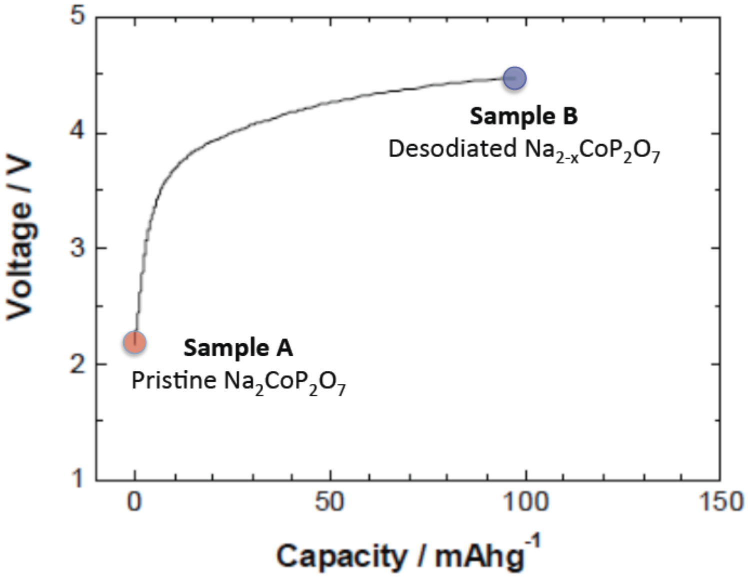


Figure S5: Comparative FT-IR spectra of pristine $Na_2CoP_2O_7$ and desodiated $Na_{2-x}CoP_2O_7$, showing clear change in the chemical bonding nature.



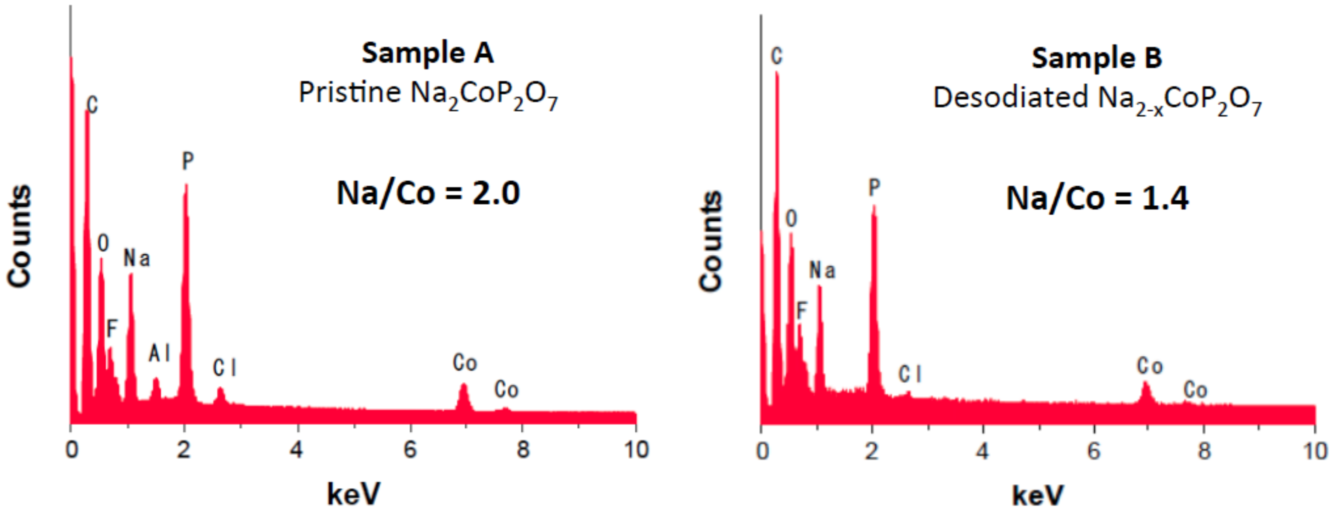


Figure S6: EDX elemental analysis of pristine $Na_2CoP_2O_7$ (sample A) and electrochemically desodiated $Na_{2-x}CoP_2O_7$ (sample B) cathodes. The decrease in Na/Co ratio from 2.0 to 1.4 confirms successful (partial) desodiation process.

**References:**

1. A. Coelho, TOPAS-Acedemic Computer Software, Coelho software, Brisbane, Australia, 2007.
2. K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **13**, 1272.