Electronic supplementary information (ESI)

Microstructure tuned $Na_3V_2(PO_4)_3$@C electrodes toward ultra-long life sodium-ion batteries

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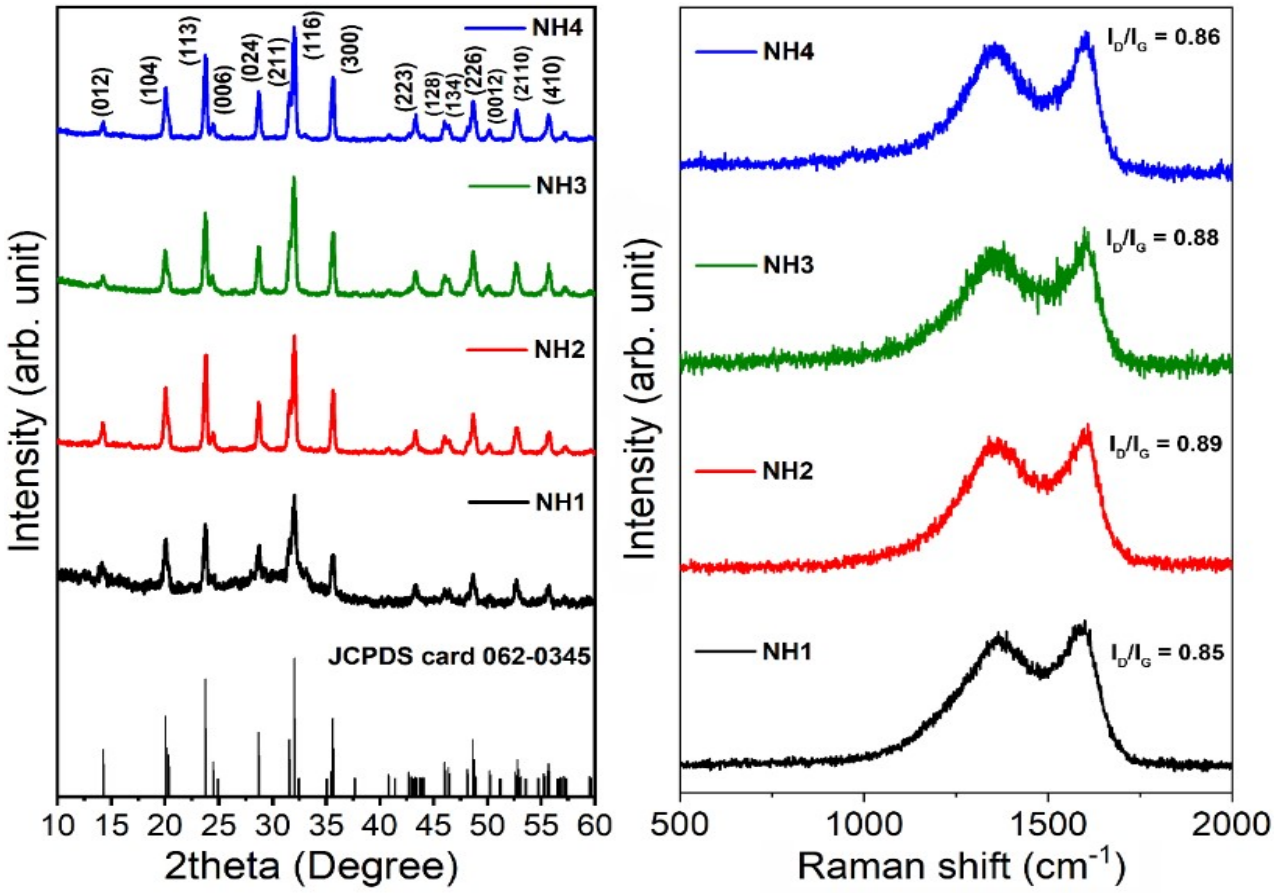

Fig. S1 (a) Powder X-ray diffraction patterns of different NVP@C samples along with the relevant JCPDS reference pattern. (b) Raman spectra of different NVP@C samples.

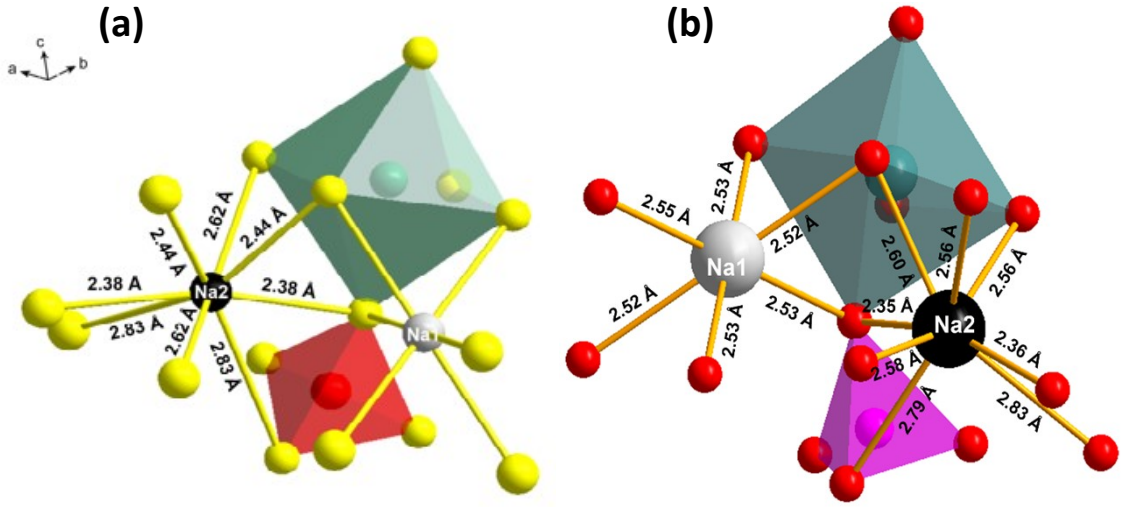

Fig. S2 (a) A representative molecular fragment showing different Na-sites and their coordination number (CN) of the standard $Na_3V_2(PO_4)_3$ (COD: 2225132), (b) $Na_3V_2(PO_4)_3$ sample calcined at 850°C.

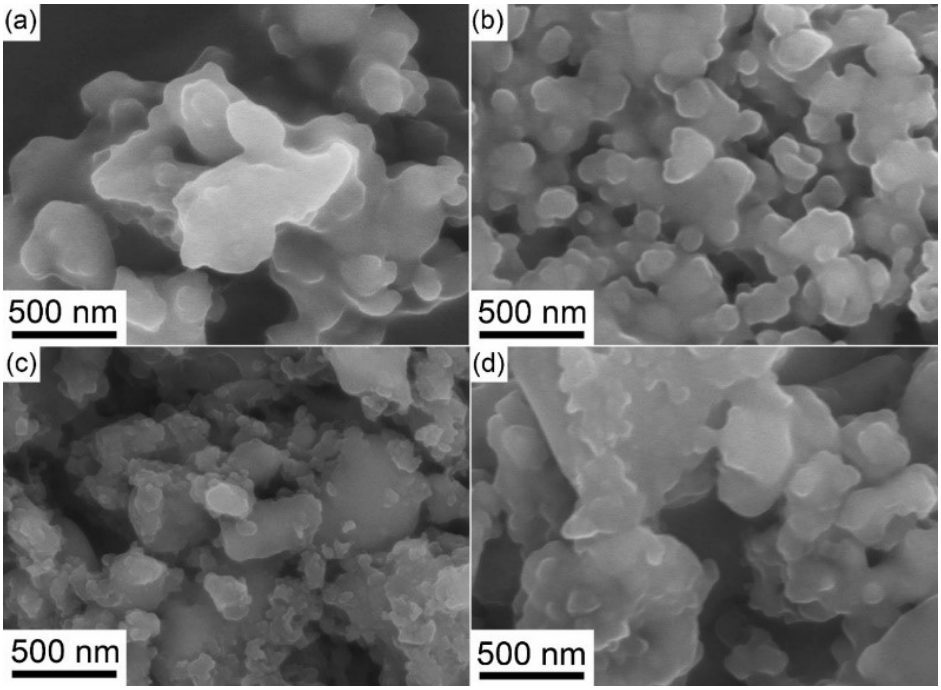

Fig. S3 FESEM images of NVP@C at different calcination temperatures: 750°C (a), 800°C (b), 850°C (c), and 900°C (d).

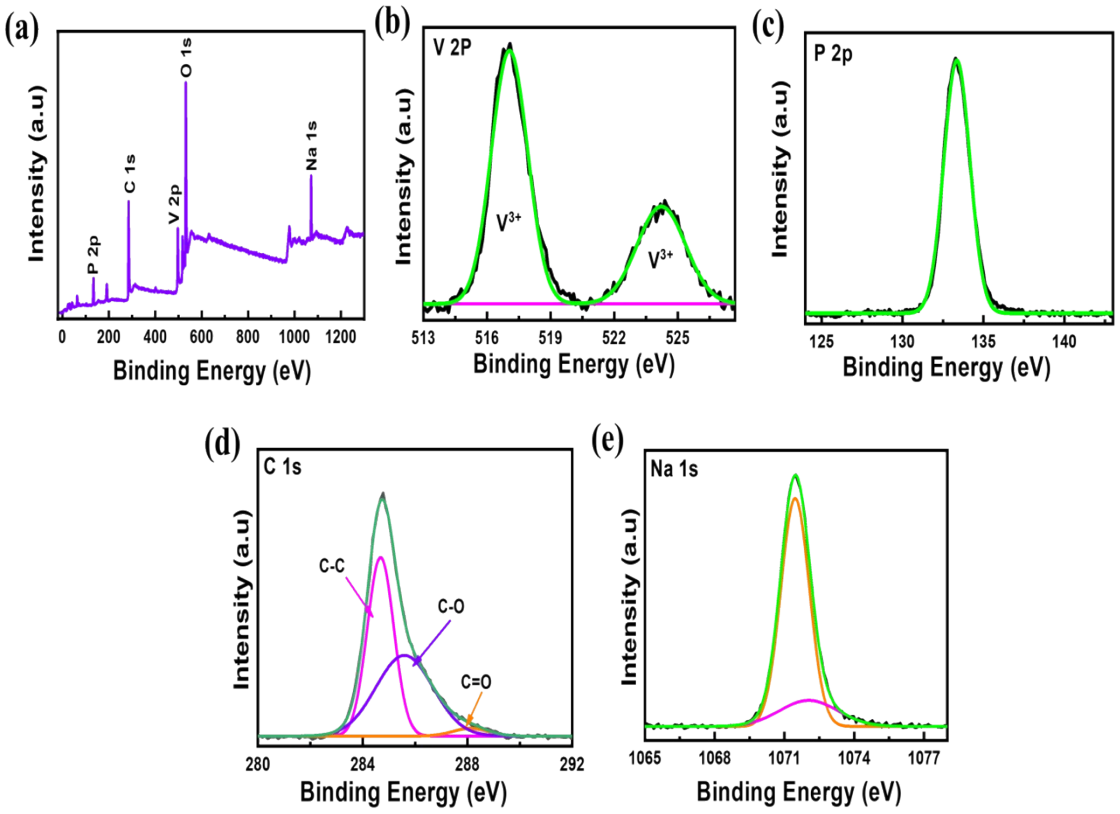

Fig. S4 XPS spectra of NVP@C calcined at 850°C (a) survey spectrum, (b) V 2p, (c) P 2p, (d) C 1s, and (e) Na 1s.

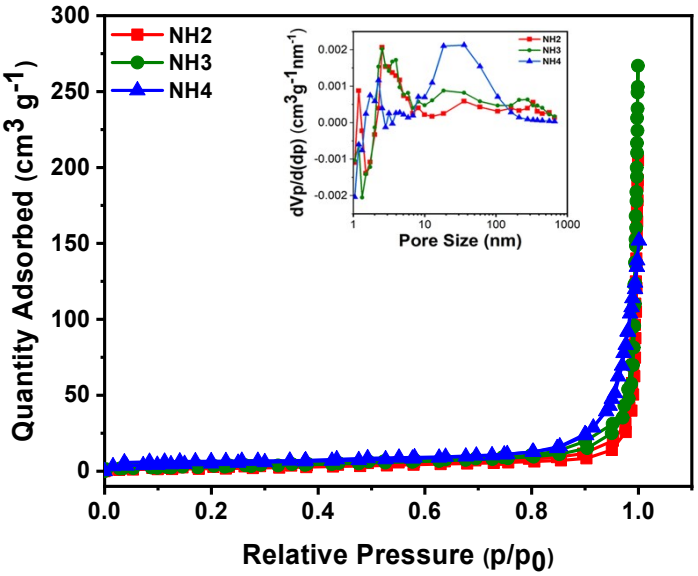

Fig. S5 N2 Adsorption–desorption isotherm of NVP@C at different calcination temperatures.

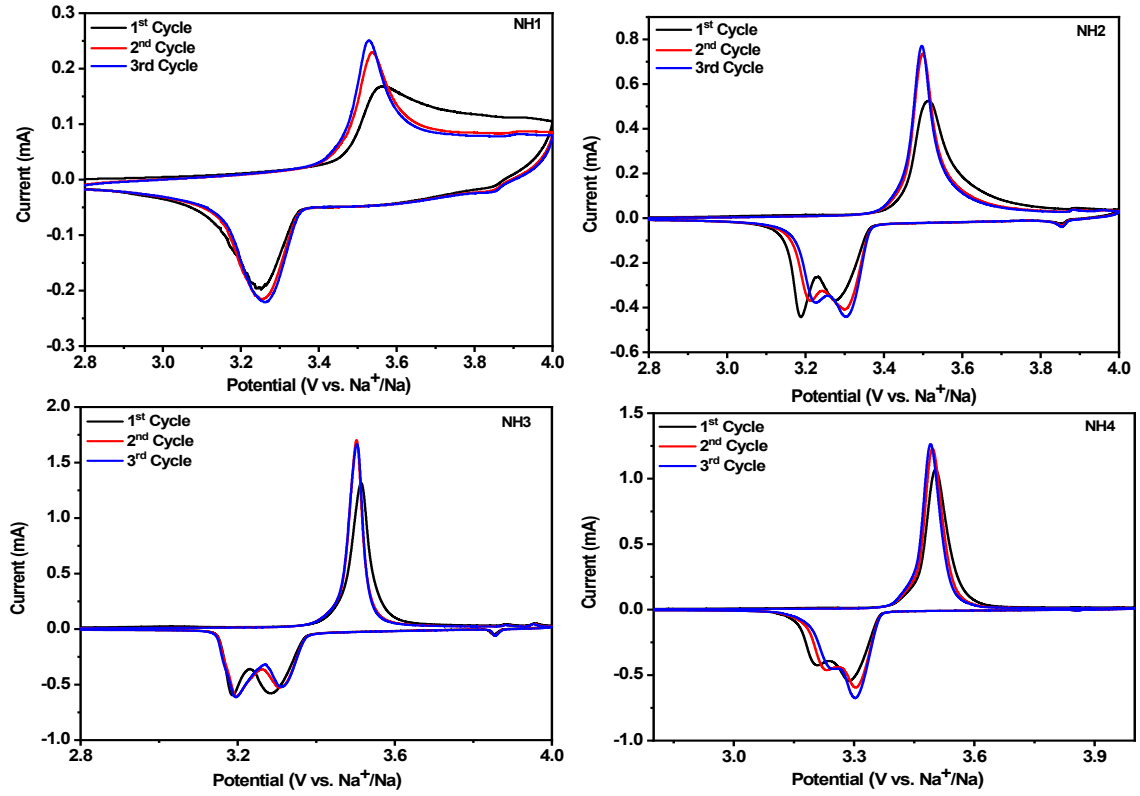

Fig.S6 CV curves of NVP@C at different calcination temperatures.

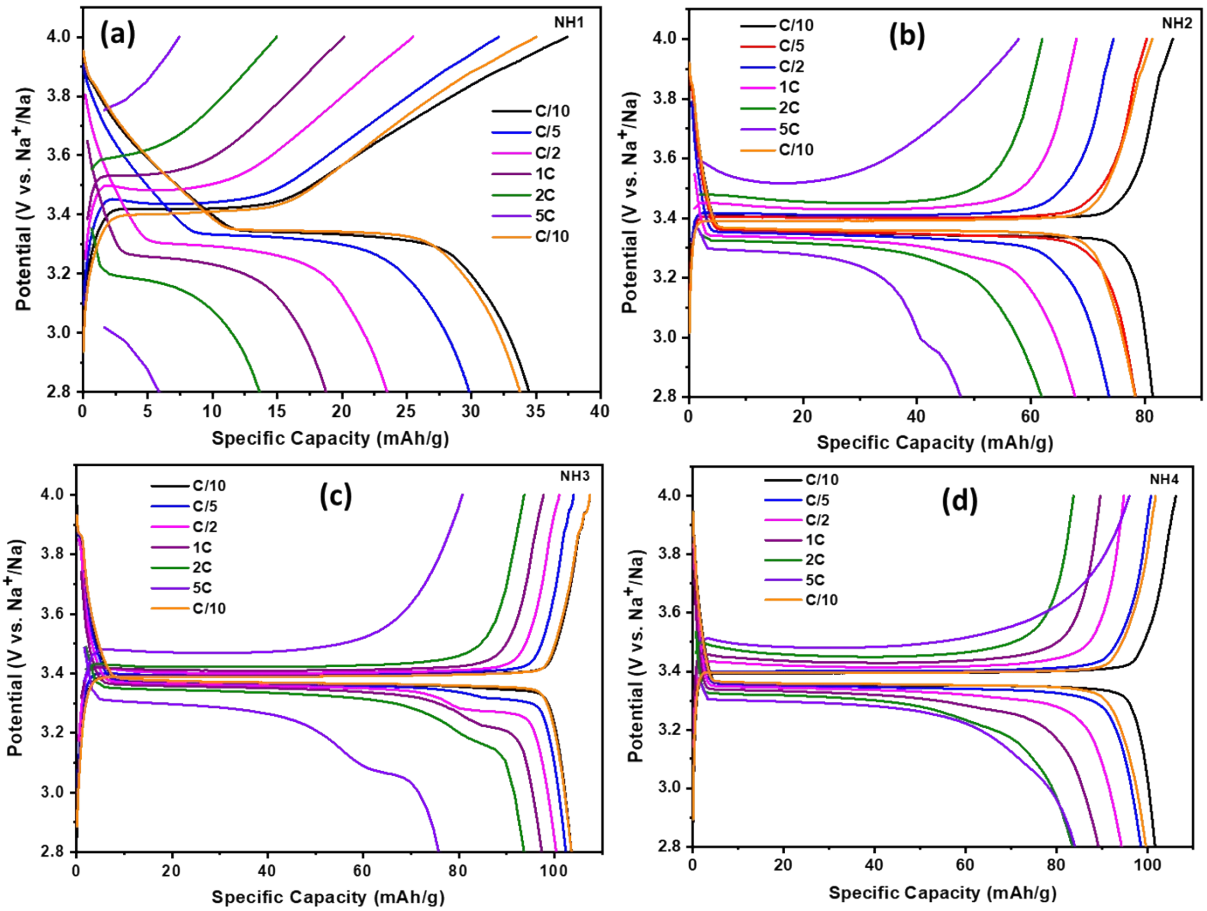

Fig.S7 The first charge-discharge profiles at different current rates of NVP@C at different calcination temperatures in a potential range of 2.8–4.0 V vs. Na/Na$^+$ (a) 750, (b) 800, (c) 850 and (d) 900°C.

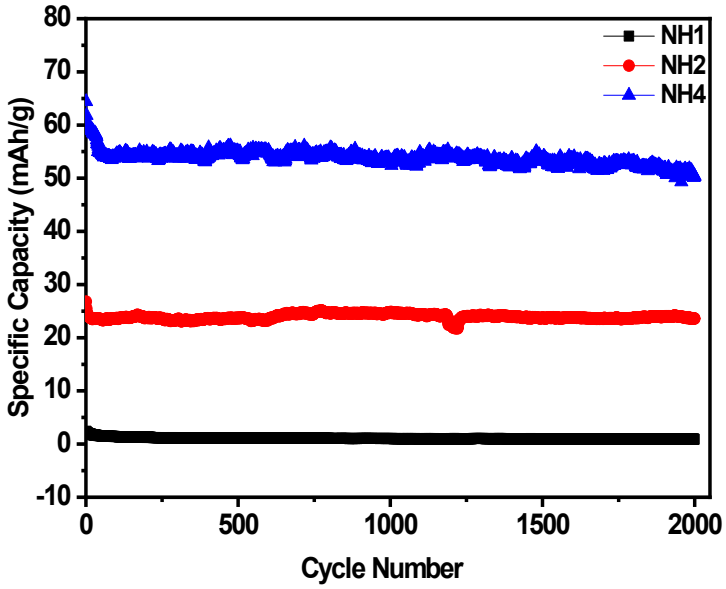

Fig. S8 Cycling performance of NVP@C calcined at 750, 800 & 900°C.

Table S1: Different crystal structure parameters used in the PXRD refinement analysis for the NH3 sample.

Symbol	Multiplicity	Wyckoff	x/a	y/b	z/c	Occupancy
Na1	6	b	0.3333	0.6666	0.1667	0.8144
Na2	18	e	0.6667	0.9838	0.0833	0.7205
O1	36	f	0.1501	0.5012	0.0830	0.9783
O2	36	f	0.5594	0.8402	0.9744	-0.0252
P	18	e	-0.0363	0.3333	0.0833	1.0481
V	12	c	0.3333	0.6666	0.0169	0.9895

Table S2. BET surface area, pore radius, and pore volume of NVP@C for different calcination temperatures.

Sample	Surface area (m^2g^{-1})	Average Pore radius (nm)	Pore Volume (cc g^{-1})
NH2	9	48	0.2254
NH3	13	46	0.3020
NH4	17	24	0.2091

Table S3. Oxidation/reduction peaks and potential differences for different calcination temperatures.

Temperature (°C)	Peak Position (V) 1st cycle		Peak Position (V) 3rd cycle		Potential difference (V) 1st cycle	Potential difference (V) 3rd cycle
	Oxidation	Reduction	Oxidation	Reduction		
750	3.55	3.24	3.52	3.26	0.31	0.26
800	3.51	3.28 & 3.19	3.49	3.30 & 3.22	0.23	0.19
850	3.51	3.28 & 3.18	3.50	3.31 & 3.19	0.23	0.19
900	3.50	3.29 & 3.20	3.49	3.30 & 3.23	0.21	0.19

Table S4. Comparison of Specific discharge capacities for the first four cycles at different C-rates and temperatures.

Temperature (°C)	Specific Capacities (mAh g^{-1})						
	C/10	C/5	C/2	1C	2C	5C	C/10
750	34	29	23	18	13	6-5	33
800	82-81	79-78	78-74	72-68	62	47-46	78
850	103	103-102	100	98-97	94-93	75	103
900	101	100-98	94	90-89	84-83	84-81	99

Table S5. The comparison of electrochemical performances of $Na_3V_2(PO_4)_3$-based cathode materials.

Electrode	C-rate	Discharge Capacity (mAh g^{-1}) (Cycle Number)	Capacity Retention	Ref.
NVP/C	10C	63	-	[1]
NVP/C	10C	62 (1) – 38 (3000)	62%	[2]
NVP/C	10C	84.4	-	[3]
NVP-C-B0.38%	10C	87 (1) – 70 (50)	80.9%	[4]
NVP/C nanowire	1C	94 (1)-20 (50)	53.2%	[5]
NVP/(C+G)	5C	95.3 (1)-88.7 (200)	92.5%	[6]
$Na_3V_2(PO_4)_3$/C	10C	≈ 40	-	[7]
$Na_3V_2(PO_4)_3$/C	10C	25	-	[8]
NVP/G	5C	86 (1)-70 (50)	70%	[9]
$Na_3V_2(PO_4)_3$/C	10C	92 (1)-72 (100)	77.8%	[10]
$Na_3V_2(PO_4)_3$/C	1C	70 (1)-50 (200)	80%	[11]
$Na_3V_2(PO_4)_3$/C	1C	100 (1)-45 (400)	45%	[12]
Br/N/a-C@NVP	10C	40 (1)-32 (500)	92%	[13]
NVP@N-HC	10C	93 (1)-67 (1000)	72%	[14]
3D NVP@C	5C	81 (1)-76 (200)	94.2%	[15]
NVP@C nanofiber	2 C	77 (4)-75 (66)	97.4%	[16]
NVP@PEDOT	1C	100 (1)-80 (200)	80%	[17]
Fe-NVP@C	5C	91 (1)-43 (400)	46.7%	[18]
$Na_3V_2(PO_4)_3$/C	10C	64 (1)-52 (1000)	81.5%	[19]
$Na_3V_2(PO_4)_3$/C	**10C**	**67 (1)-63 (2000)**	**94%**	**Current Work**

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