
실리콘계 탄소복합체 음극

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Anode materials

- **Graphite** – commonly used as anode material for Li-ion batteries.
 - Maximum theoretical specific capacity is 372 mAh/g (or 840 Ah/L)
 - To increase the specific capacity, new anode materials are needed
- **Tin-based Composite Oxide (TCO, Fuji Photo Film Co, Ltd, Japan)**
 - Capacity : 2600mAh/cm³, 650mAh/g
 - Good cyclability (> 500 cycles)
 - Problem
 - large irreversible capacity : ~ 40% (SnO + 6.4Li → Sn + Li₂O + 4.4Li)
- **Nano-Sized transition-metal oxides(NiO, FeO, Cu₂O, CoO, Co₂O₄)**
 - $\text{CoO} + 2\text{Li} \rightleftharpoons \text{Li}_2\text{O} + \text{Co}$
 - Capacity : 700~ 1000mAh/g
 - Irreversible capacity : ~25%
 - High average voltage : ~1.8V



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Alloy anode materials

■ Lithium Alloys : Li_xM (M=Sn, Si, Al, Sb etc)



- High capacity
- Low irreversible capacity

Problems

- Large volume change (100 – 700%)
- Poor cyclability

Discharged species	Charged species	Voltage (vs. Li/Li ⁺)	Capacity (mAh/g)	Volume Increase (%)
Al	LiAl	0.36	993	97
Sn	Li ₂₂ Sn ₅	0.50	993	676
Si	Li ₂₂ Si ₅	0.40	4200	322
Pb	Li ₂₂ Pb ₅	0.49	570	233

■ Approach

Active/inactive composite (alloy)

- buffering inactive elements
- enhanced cyclability



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Scopes of this study : 실리콘계 탄소복합체

■ M-Si 합금 / 탄소복합체

- M-Si alloys
- M-Si alloys / graphite composites
- Carbon-coated M-Si alloys / graphite composites

■ Si 분산산화물 / 탄소복합체

- Nano-Si / oxides
- Nano-Si-oxides-graphite composites
- Carbon-coated nano-Si-oxides / graphite composites



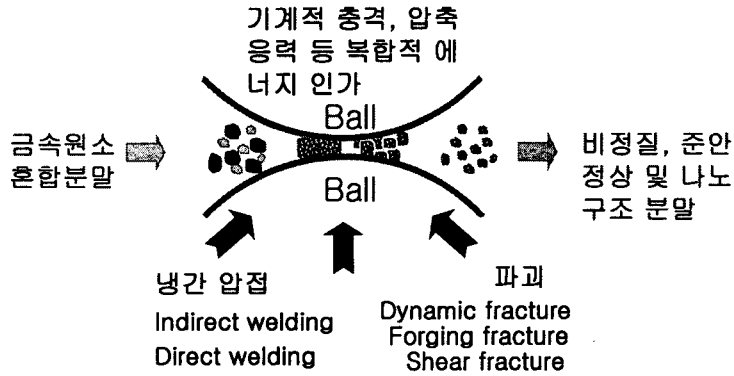
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Mechanical Alloying

Non-equilibrium, Supersaturated solid solution, Amorphous, Nano-quasicrystalline, Nano-powder



(cf.) Mechanochemical reaction

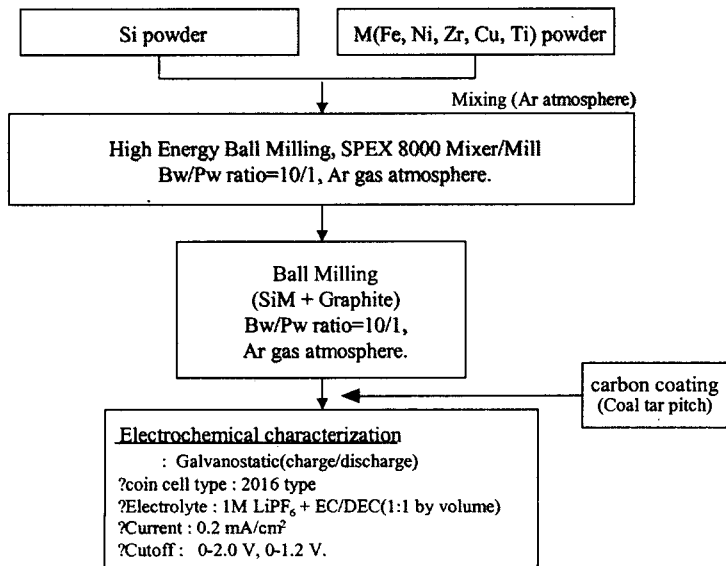


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M-Si Alloys/탄소복합체



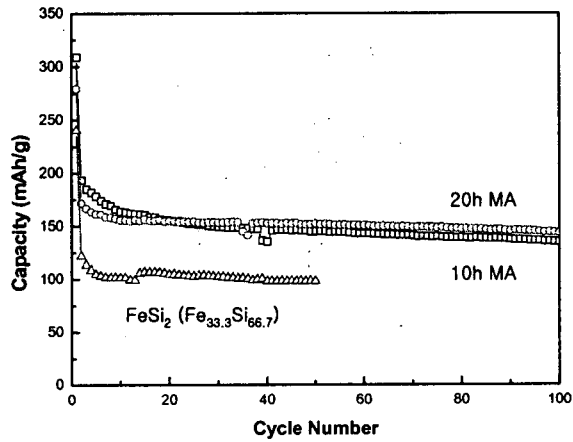
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Fe₂₃Si₇₃(FeSi_{2.7}) systems

Cyclability of Fe₂₇Si₇₃ alloys



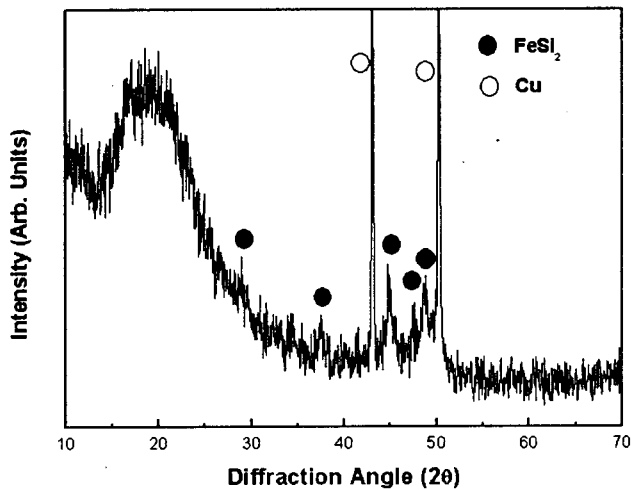
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Fe₂₃Si₇₃(FeSi_{2.7}) systems

XRD patterns of Fe₂₃Si₇₃ electrode milled for 20h after 100 cycles



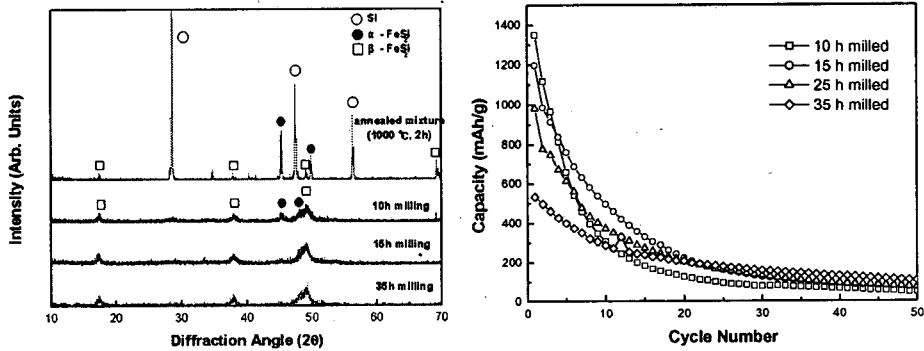
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Fe₂₀Si₈₀(FeSi₄) systems

XRD patterns & Cyclability of Fe₂₀Si₈₀ alloys after annealing and ball-milling

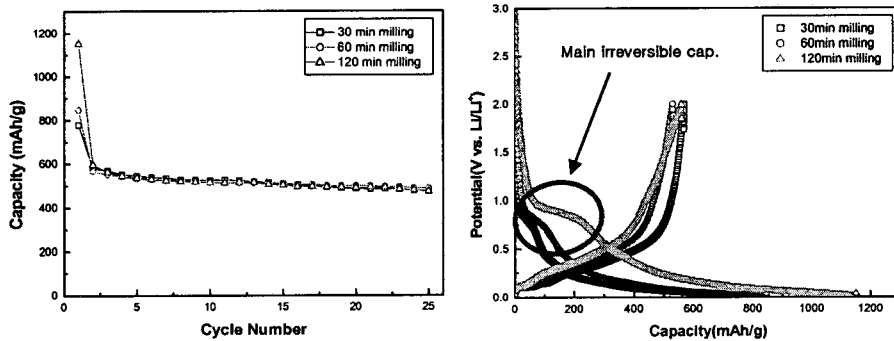


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Fe₂₀Si₈₀/graphite composite

Cyclability & 1st Discharge and charge curves

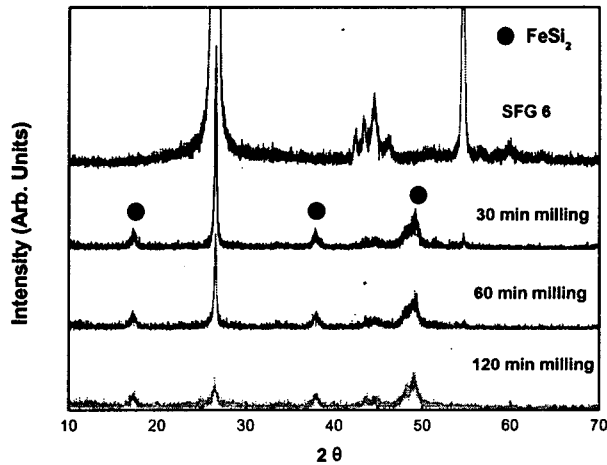


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Fe₂₀Si₈₀/graphite composite

XRD patterns of ball-milled Fe₂₀Si₈₀/graphite composites



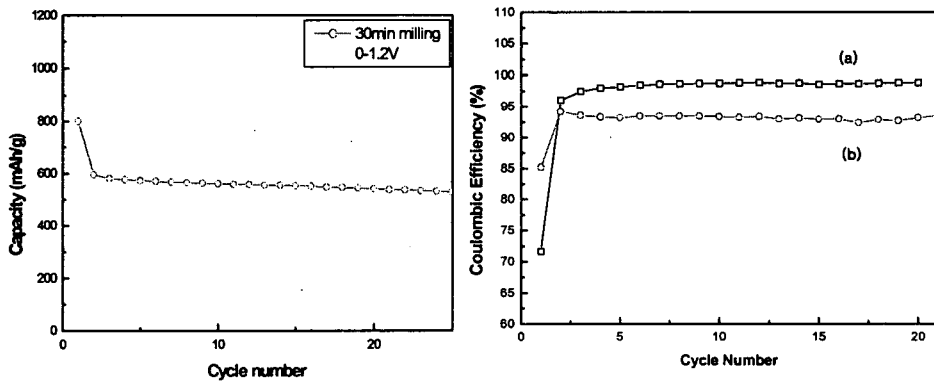
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Fe₂₀Si₈₀/graphite composite

Cyclability & Coulombic efficiency of ball-milled Fe₂₀Si₈₀/graphite composites



(a) 30 min ball-milled Fe₂₀Si₈₀/graphite alloy composite electrode
(b) Fe₂₀Si₈₀ alloy electrode

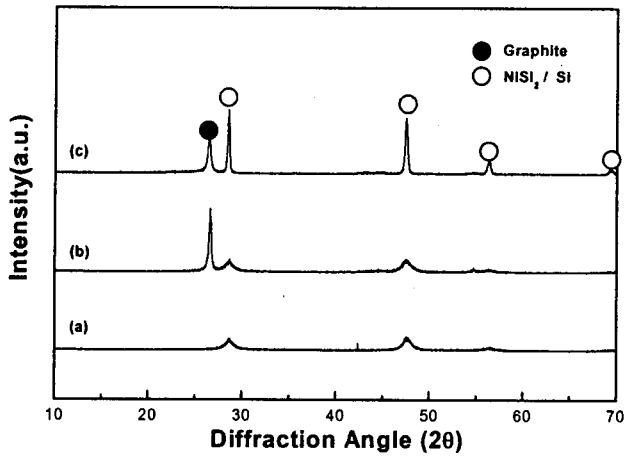


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Ni₂₀Si₈₀/graphite composite



(a) Ball-milled Ni₂₀Si₈₀ (b) Ni₂₀Si₈₀ / graphite composite
(c) Carbon-coated Ni₂₀Si₈₀ / graphite composite



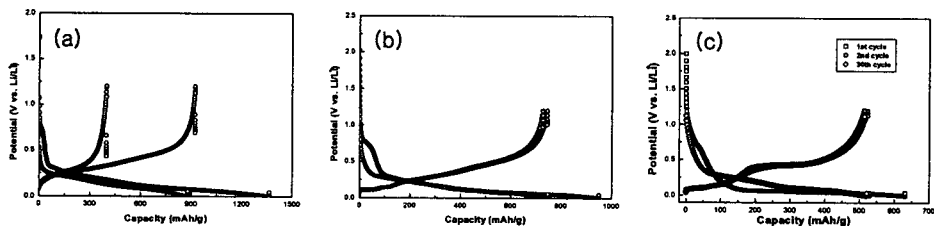
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Ni₂₀Si₈₀/graphite composite

Charge - Discharge curves.



(a) Ball-milled Ni₂₀Si₈₀
(b) Ni₂₀Si₈₀ / graphite composite
(c) Carbon-coated Ni₂₀Si₈₀ / graphite composite



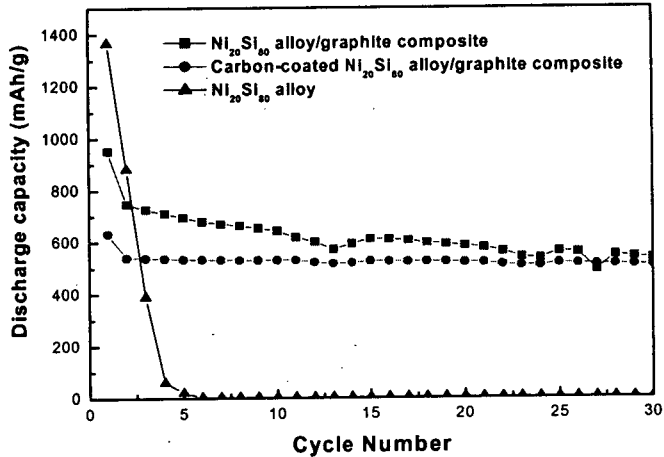
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Ni₂₀Si₈₀/graphite composite

Cycling performance

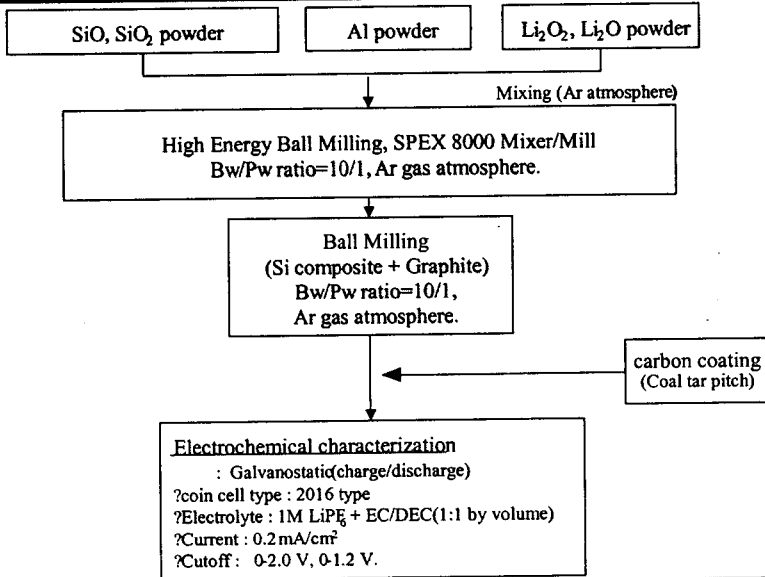


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Nano Si-oxide/탄소복합체



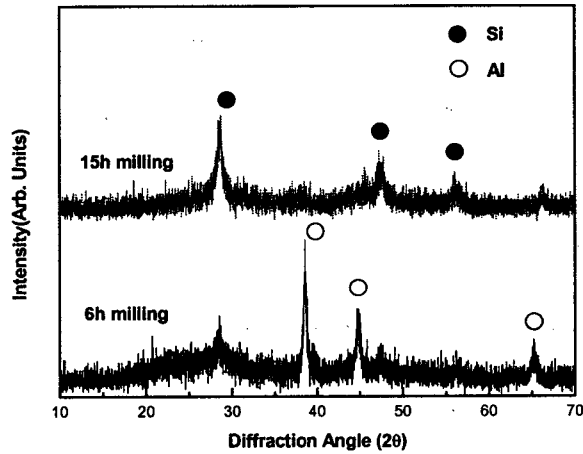
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SiO

XRD patterns of SiO:Al: Li₂O = 1:1:0.2 composites milled for 6 and 12h

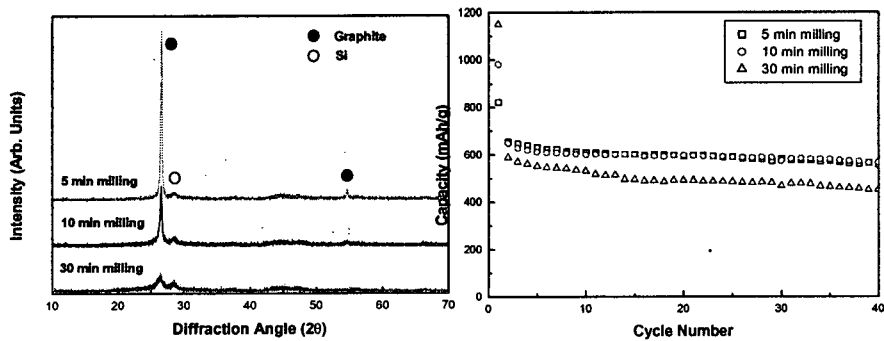


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Nano-Si dispersed Oxide(SiO)/graphite composite

XRD patterns & Cyclability

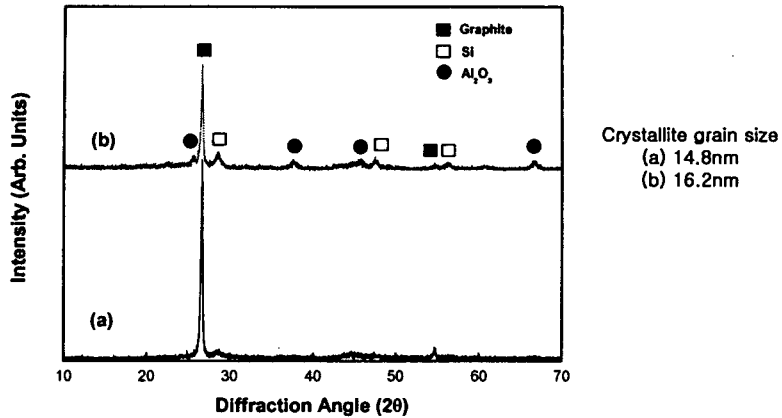


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Carbon coated Nano-Si dispersed Oxide(SiO)/graphite composite

XRD patterns



(a) nano-si dispersed oxide/graphite composite (5 min milling)

(b) carbon coated nano-si dispersed oxide/graphite composite (70 wt.% coal tar pitch, 900°C for 1h in Ar)



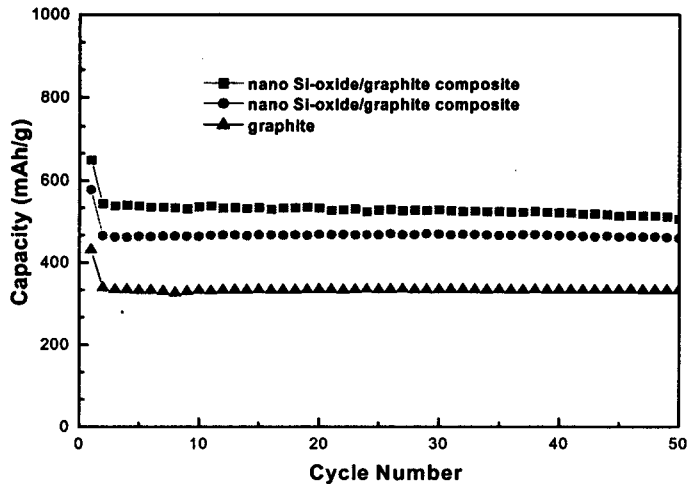
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Carbon coated Nano-Si dispersed Oxide(SiO)/graphite(SFG6) composite

Cyclability



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결론

탄소코팅된 M-Si 합금/흑연복합체 및 Nano Si-산화물/흑연복합체의 경우 고용량의 특성과 함께 우수한 싸이클 특성 및 낮은 초기 비가역용량을 나타낸다.



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