Advances in plasma sprayed silicon nanoparticles for next generation lithiumion batteries

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Abstract: Silicon nanoparticles have been produced by plasma spray with metallurgical silicon powders and their feasibility as anode of lithium-ion battery is evaluated. With the recently developed plasma spray system, Si nanparticles with - 250 nm are produced at the rate as fast as 25 g/min. These Si nanoparticles are confirmed to attain reasonably high cycle capacity both in all-solid-state battery and organic-liquid electrolyte batteries. Nanoparticles with modified structure can be produced by optimizing the co-condensation during plasma spray and exhibited an improved battery performance.

Keywords: plasma spray, silicon nanoparticles, lithium-ion battery.

1. Introduction

Plasma spray is widely recognized as the industrial coating technique. The term "spray" however means literally "spray materials" and does not necessarily limit the material and the product. This allows us to consider "plasma spray" in a broad sense as the general term of the industrial process to inject continuously material at either vapor, liquid or solid state into the plasma and transform the material chemically and/or physically with the plasma characteristics [1]. With this redefinition, opportunities of the plasma spray technique will be widely opened and radical advancements is also anticipated in a variety of applied fields. One example of the opened opportunity of plasma spray is nanoparticles for high density electrodes of the next generation lithium-ion batteries.

In the roadmap to the carbon-neutral society at 2050, significant electric vehicle (EV) shift is planned as governmental policy worldwide. The general target is to replace the present fossile fulel cars by EV 100% in new car market at 2030. To make this trend possible, adequate amount of rechargeable batteries needs to be produced and the materials for batteries have to be available. According to the recent estimates of the material requirements for the battery [2], silicon as the promising candidate for anode of the next generation lithium-ion battery is expected to be required 30 times at year 2030 than the amount used at 2020; this number increases to even 250 times at year 2050. Point is that any silicon is not good enough for battery. Silicon has to be processed to be nanosized and also be structured to attain satisfactory battery performance. In brief, silicon possesses nearly 10 times higher theoretical capacity than the conventional graphite, but it will change the structure and dilate the unit volume up to 400% during (de)lithiation battery reaction, which causes the pulverization and immediate decay of the capacity in a short battery cycles. Nanoparticles and the composite structure with added functionalities, such as surface stabilization and electric conducting paths, are known to mitigate these difficulties [3-6]. Therefore, these structured nanoparticles are to be produced at amounts that meet the battery industrial forecast.

2. Comparison of silicon nanoparticles production techniques

For this mass production of silicon nanoparticles, plasma spray is advantageous and competitive in terms of cost and throughputs. For plasma spraying, we can use low cost metallurgical grade powders at the market price of \$2-3/kg, which contrats to the Si gas source, such as trichlorosilane and monosilane, at the price of approximately \$5,000-10,000/kg used for the chemical vapor deposition. Another conventional approach is mechanical milling/alloying. It uses a simple rolling pot and mixes the raw powders with hard balls for a long time. It requires only several 100W for operation. However, to make hard silicon materials to be several 10 nm in size, we have to operate nearly one month. Also, to apply adequate mechanical energy to powders, limited amount of raw powders can only be loaded in a pot. As a result, the overall energy required to produce



Fig. 1. Newly developed plasma spray system (inverter power unit and hybrid plasma torch).



Fig. 2. Size and oxygen content of silicon nanoparticles produced by plasma spray.

nanoparticles with 100 nm at 1kg reaches 518 kJ/g, which is far greater than 168 kJ/g required for the plasma spray. With the newly developed plasma system (Fig.1) equipped with hybrid plasma torch, inverter power unit and high yield nanoparticle collection flunge, we can produce nanoparticles at rates as fast as 1.5 kg/h continuously for 2 hours with no maintenance [7]. Furthermore, the unit time to produce 1 kg of 100 nm nanoparticles is 0.67 h/kg, which is far less than 720 h/kg for mechanical milling system. Therefore, plasma spray now a days is a strongest candidate for silicon nanoparticle production and can also be selected as carbon-offset technologies.

3. Silicon nanoparticle characteristics and its feasibility as high density battery anode

With plasma spray system, we can control the size of the nanoparticles by changing the raw powder feed speed. As is seen from Fig. 2, the oxygen content x in SiO_x representation increasese with decreasing the average particle size, and this variation coincides reasonably with the change in the BET surface area. This indicates that the oxidation occurs specifically on surface of the particles and the oygen content increases significantly for smaller nanoparticles. Fig. 3 compares the cycle capacity of the allsolid-state battery using various silicon nanoparticles. While relatively large silicon particle shows rapid decay of the capacity, smaller particles maintains relatively higher capacity. The capacity of the smallest particles however reduces the initial discharge capacity. It is therefore clear that the nanoparticles have to be smaller than 150 nm to avoid initial rapid capacity decay. Oxygen reacts with lithium easily and form stable phase materials in the lithium-ion battery, which reduces the initial efficiency and the reversible capacity. oxidation of nanoparticle, therefore, needs to be treated carefully if high capacity and high cycle stability are to be attained simultaneously. Recently, we have demonstrated that the oxidation can be suppressed even for nanoparticles as small as 20 - 40 nm, if one pays appropriate attentions to the reactor environment immediate after the nanoparticle growth by plasma spray before collecting the particles [8].

If the secondary element M powder is fed into plasma together with silicon, both Si and M vaporise immediately and form high temperature alloy vapor in the plasma. Upon cooling at the tail flame, the M element will attach onto Si nanoparticles via heterogeneous nucleation during cocondensation, forming eventually composite structure. Interestingly, as is seen in Fig. 4, the structure can be tuned by the cooling speed during nanoparticle growth, that is, the epitaxial interfaces is created at slow speed [9,10]. This structure reinforces silicon nanoparticle against fracture during reaction and adds electric-conducting network in the anode, resulting in an enhanced battery cycle capacity and cyclability (Fig.5).

4. Conclusion

With a recent advancement in the plasma torch, power unit, specific reactor design dedicated for nanoparticle







Fig. 5. Comparison of the cycle capacity of the cell using different Si:Ni nanoparticles.

production and careful control of material condensation, plasma spray is now becoming a competitive technology both in product quality, production throughputs and production cost and energies. It is therefore anticipated that this process is selected as the leading production technique for the materials of the future lithium-ion batteries.

5. References

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