Supplementary Information

Cathodic Corrosion: An Electrochemical Approach to Capture Zintl Compounds for Powder Materials

Authors: Yingchang Yang,[a] Binghan Qiao,[b] Zhengping Wu[a] and Xiaobo Ji[a] *

Affiliations:

[a]Key Laboratory of Resources Chemistry of Nonferrous Metals, Ministry of Education, College of Chemistry and ChemicalEngineering, Central South University, Changsha 410083, China.

*E-mail: xji@csu.edu.cn;

[b]School of Foreign Languages, Central South University, Changsha 410083, China.

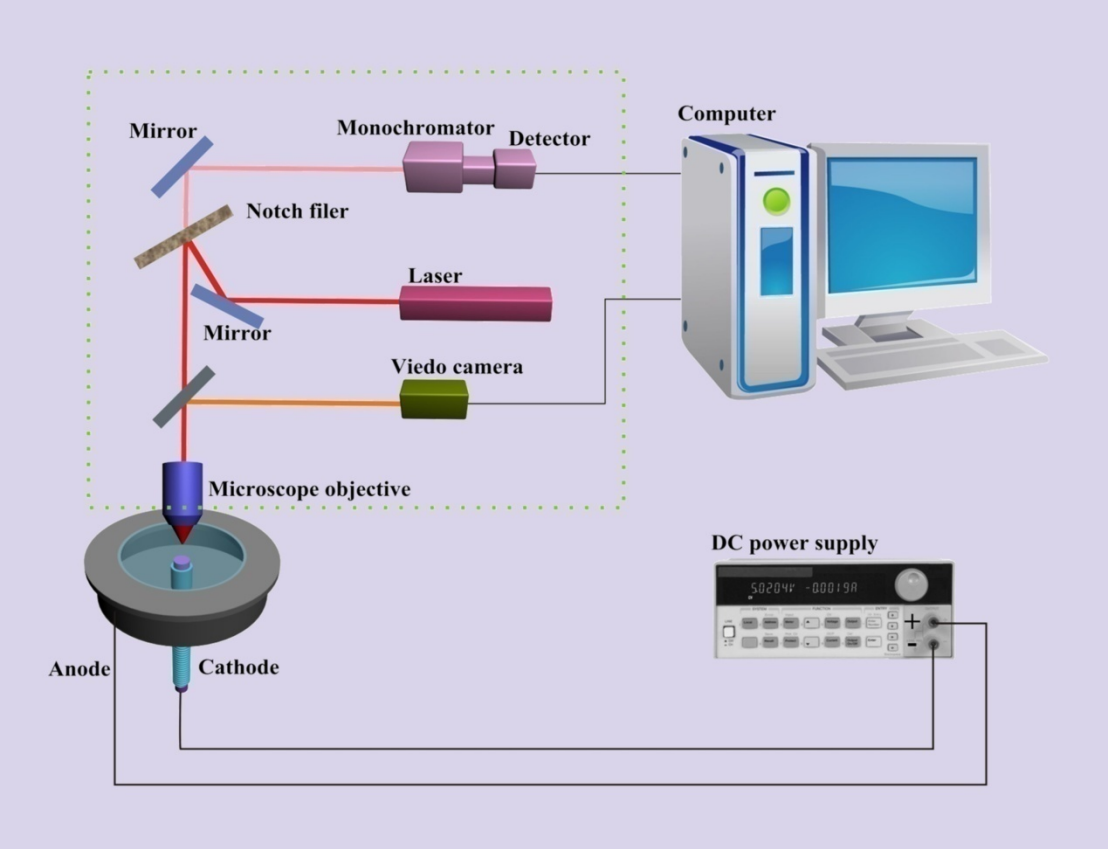

Figure S1. Experimental setup made up of four parts for *in situ* Raman spectroscopy, which includes a Raman spectroscopy instrument (left-top corner), a computer, a DC power supply and a sealed electrochemical cell (left-bottom corner).The electrochemical cell is water-tight realized with an O-ring design. In which, Pt ring and the Sn/Pb rods were used as the anode and cathode, respectively. The surface of the cathode was orientated upwards to allow efficient Raman measurements and an optically transparent quartz was used to protect the solution and electrode from being interfered by the ambient atmosphere.

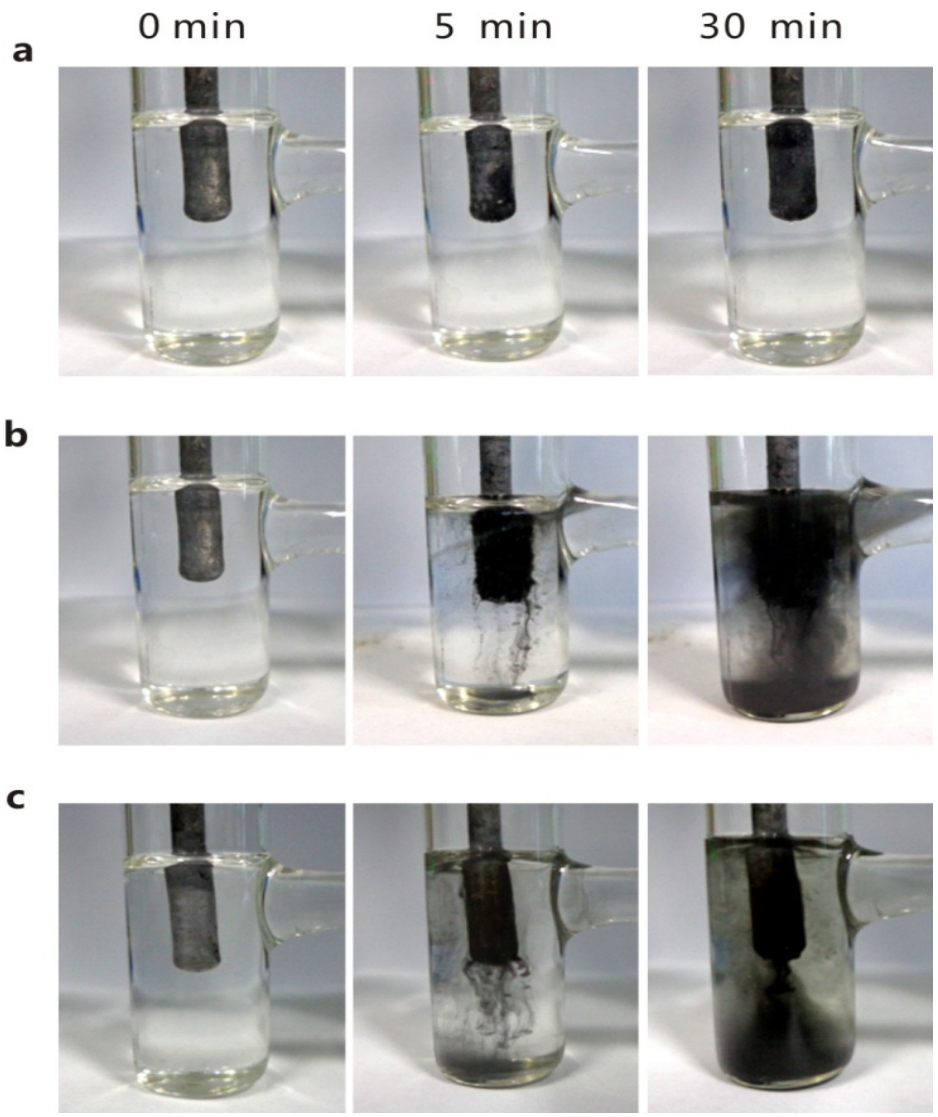

Figure S2. Photos of cathodic corrosion of Pb in 0.1 M DMF solutions of (**a**) TMAP, (**b**) TEAP and (**c**) TBAP for different minutes.

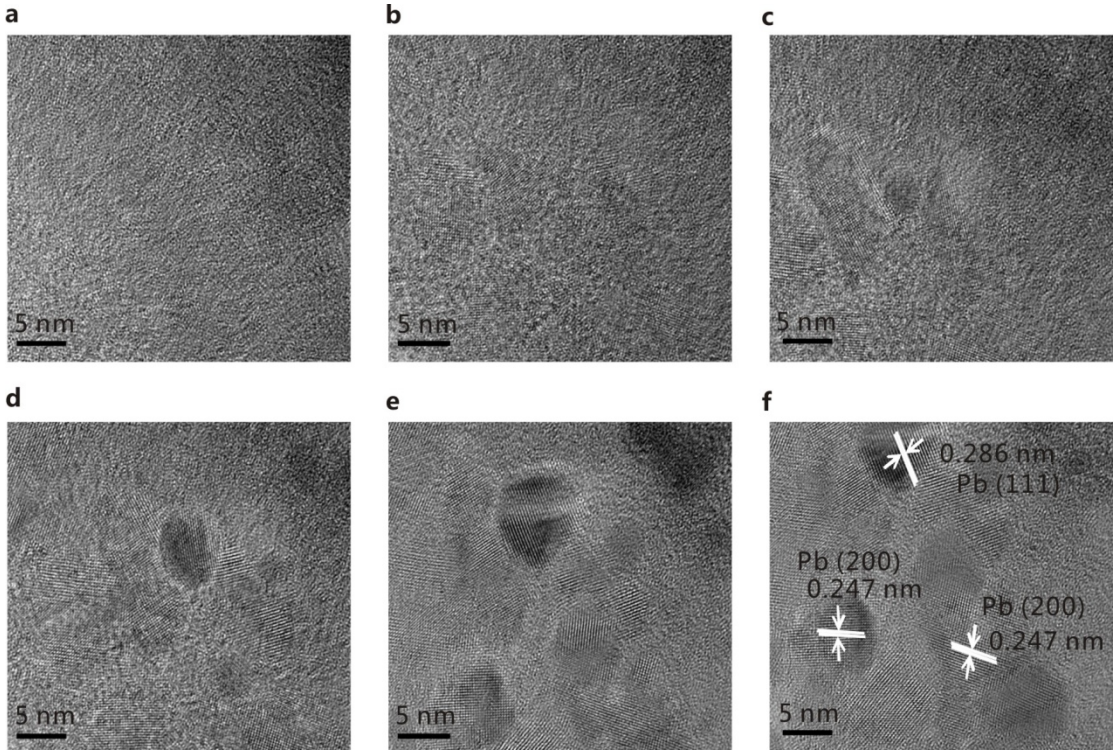

Figure S3. HRTEM of sheet-like Pb powder under the action of electron beams for 0, 10, 30, 60, 90 and 120 s. The Pb powder with poor crystallinity can be gradually converted into nanocrystalline material.

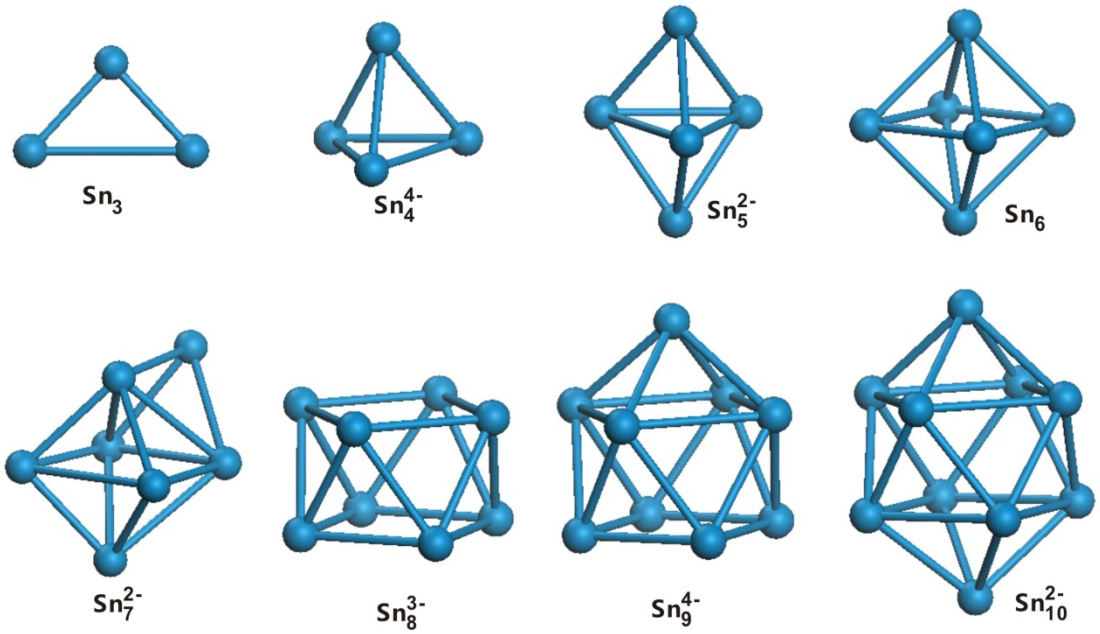

Figure S4. The quantum chemically optimized structure of Sn_x^{y-} (x = 3 to 10) clusters obtained by DFT at the B3LYP/LanL2dz basis.

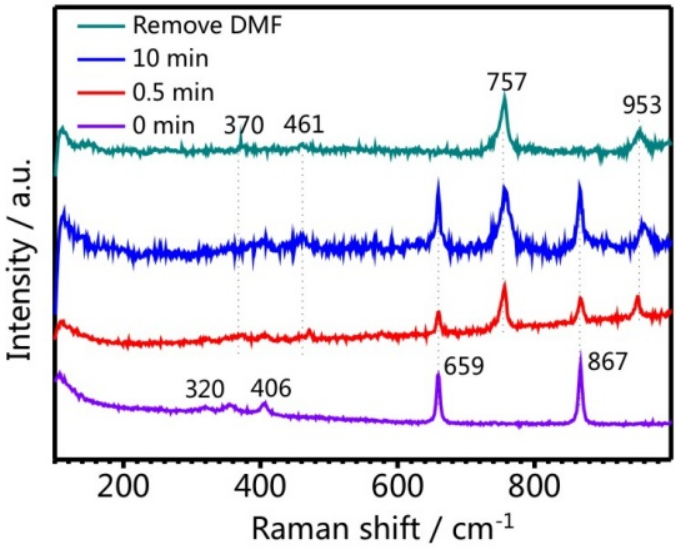

Figure S5. *In situ* Raman spectroscopy of the as-generated Zintl compound $[(CH_3)_4N^+]_4Pb_9^{4-}$ on the top surface of Pb electrode during cathodic polarization for different minutes. For comparison, the Raman spectra of Pb electrode in the electrolyte solution before cathodic polarization and the as-generated Zintl compound $[(CH_3)_4N^+]_4Pb_9^{4-}$ after being removed the DMF were also shown.

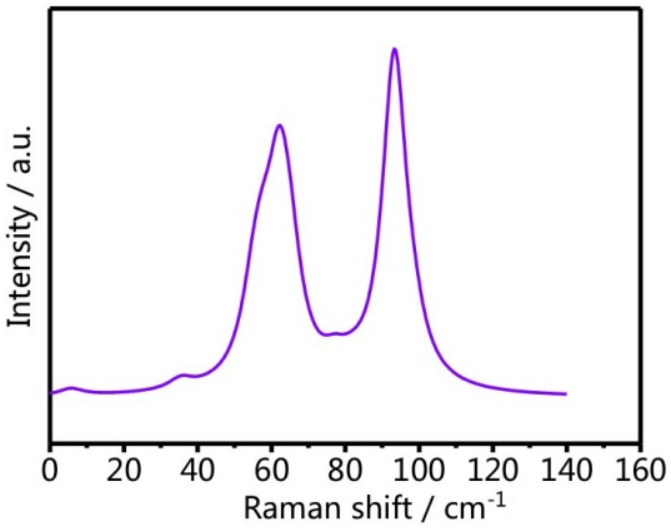

Figure S6. Calculated Raman spectra of Pb_9^{4-}cluster.

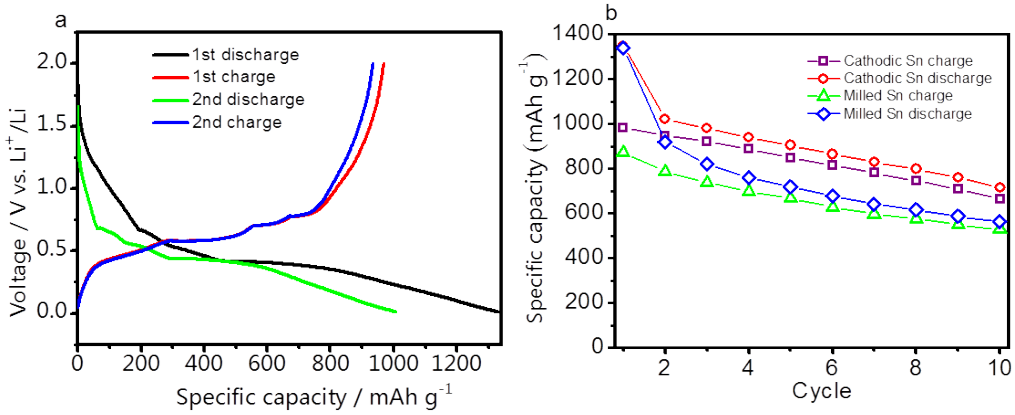

Figure S7. (a) Galvanostatic charge–discharge profiles of the first and the second cycles of the Sn electrode. (b) Cycling performance of the Sn electrodes at 100 mA g^{-1}.

Table S1. Physical properties of group 14 elements[1,2].

Substance	Classification	Electrical Resistivity / Ω m(at 25 °C)	Enthalpy of Atomization / kJ mol^{-1} (at 25 °C)	Bonding Type	Crystal Structure	Melting Point/ °C
Diamond	Non-metal	10^{18}	—	Covalent	Cubic Face-Centered	3550.0
Graphite	Non-metal	16.4×10^{-6}/	—	Covalent/Van der Waals forces	Hexagonal	3500.0
Si	Metalloid	2.5×10^{-5}	439.32	Covalent	Cubic Face-Centered	1410.0
Ge	Metalloid	0.5	376.56	Covalent	Cubic Face-Centered	937.4
Sn	Other Metals	11.0×10^{-8}	301.25	Metallic	Tetragonal	231.9
Pb	Other Metals	19.2×10^{-8}	194.60	Metallic	Cubic Face-Centered	327.5

References

1. Lide, D.R., Ed.*CRC Handbook of Chemistry and Physics*, 90th ed. (CRC Press: Boca Raton, FL, 2010)

2. Bentor, Yinon. Chemical Element.com Jan. 6, 2014<http://www.chemicalelements.com/elements/ge.html>.